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THE TWO PHTHALOXIMES AND SOME OF THEIR DERIVATIVES

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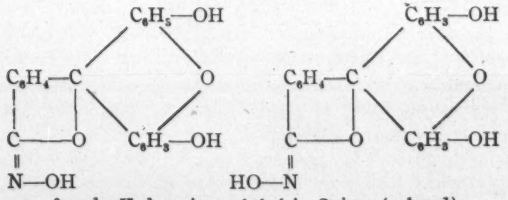
This investigation was undertaken in connection with the study of the oximes of the phthaleins. Phenolphthalein oxime has a marked yellow color and we have found that the oximes of thymolphthalein and of tetraiodo- and tetrabromophenolphthalein are also yellow, while those of phenoltetrachlorophthalein, of tetraiodophenoltetrachlorophthalein and of the trimethyl ether of tetrachlorogallein are red. Other oximes of the phthaleins are also colored. Friedländer[1] states that *o*-cresolphthalein oxime is yellow, and Richard Meyer[2] that two of the three oximes of hydroquinonephthalein discovered by him are yellowish brown, the third being *colorless*.

To these two *colored* oximes, which Meyer regards as stereoisomeric, he gives the following formulas:

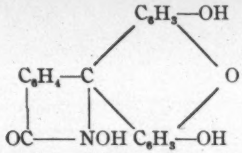


β- and γ-Hydroquinonephthalein Oximes (colored)

[1] Ber. d. chem. Ges., **26**, 2258.

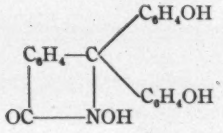
[2] *Ibid.*, **38**, 1318; **42**, 2825.

while he assigns a different structure to the colorless oxime:

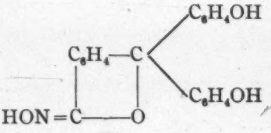


α-Hydroquinonephthalein Oxime (colorless)

For phenolphthalein oxime Meyer has suggested at various times two formulas:



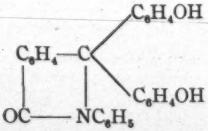
and



I II

Phenolphthalein Oxime

though in his more recent paper he seems to prefer the latter (II), mainly on account of the color of the oxime and the fact that it is so easily reduced, whereas the anilide of phenolphthalein,



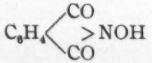
and the *colorless* α-hydroquinonephthalein oxime (see above), which have structures similar to Formula I, do not undergo reduction.

The chromophore in these *colored* oximes, according to Meyer, is the group >C=NOH, though he gives no example of *colored* compounds containing this group in a *five-membered ring*. Before taking up the question of the constitution of the oximes of the phthaleins it was thought desirable to study some simpler compounds having a structure similar to that given to the *colored* oximes by Meyer; in other words, to see if

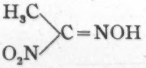
the group >C=NOH did not act as a chromophore when present in a *five-membered ring*.

The compound known as phthalylhydroxylamine, but which we will call phthaloxime, first described by Lassar-Cohn,[1] seemed best suited for the purpose, as there are no phenol residues present in this substance and therefore no possibility of the color of the compound (provided that it be colored) being due to the *quinoid* condition in one of these groups.

It is somewhat difficult to say from the literature whether phthaloxime is colored or not. In one place Lassar-Cohn[2] calls attention to its resemblance to the nitrolic acids:

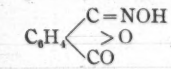


Phthaloxime

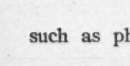


Ethylnitrolic Acid

and says that both substances, though *colorless*, turn red with a trace of alkali. In another place[3] he states that after repeated crystallization phthaloxime forms a faintly *yellow* powder. As Lassar-Cohn made his product by the action of phthalyl chloride on hydroxylamine, the unsymmetrical formula,



, would be more in accord with the views held at present regarding the structure of phthalyl chloride and would bring out, even better than his formula does, the resemblance of phthaloxime to the nitrolic acids. Attention should also be called to the fact that ethylnitrolic acid has a light yellow color. Like the nitrolic acids, phthaloxime is an acid, strong enough to decompose carbonates, and all its salts are markedly *colored*.

B. Lach[4] made phthaloxime by the action of hydroxylamine on phthalic anhydride, a method similar to that by which the phthalein oximes are made. He found that lactones, such as phthalide,  , and phthalylacetic acid,

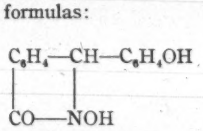
[1] Ann. Chem. (Liebig), **205**, 295 (1880).
[2] *Ibid.*, p. 312.
[3] *Ibid.*, p. 296.
[4] Ber. d. chem. Ges., **16**, 1781 (1893).

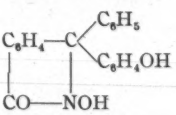
$C_6H_4\begin{cases} C=CHCOOH \\ >O \\ CO \end{cases}$, do not react with hydroxylamine.

Errera[1] also made the compound by the action of hydroxylamine on phthalic anhydride. He calls attention later[2] to the fact that phthaloxime and all of its salts are *colored* while succinyl- and camphorylhydroxylamines and their salts are *colorless*, hence he assigns the unsymmetrical formula (see above) to the first and the symmetrical structure to the other two derivatives of hydroxylamine.

In 1895 Jaubert[3] made naphthaloxime from naphthalic anhydride and hydroxylamine. He gives the product the symmetrical formula $C_{10}H_6\begin{cases} CO \\ >NOH \\ CO \end{cases}$ and states that it is colorless and forms colorless ethers, but that its metallic salts are colored.

R. Meyer[4] made the oximes of hydroxyphenylphthalide and of hydroxydiphenylphthalide, to which he gives the following formulas:

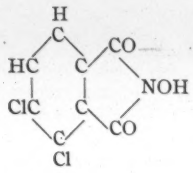




The first he describes as colorless, but the second was obtained as a yellow precipitate looking like phenolphthalein oxime. It crystallized from ether in *colorless* cubelike crystals but from alcohol in *yellow* crystals, which, however, give colorless crystals from ether and have the same melting point as the colorless product. On standing in the air for some time the colorless crystals become yellow.

Villiger[5] has recently made the 3,5-dichlorophthaloxime, to which he gives the following structure:

[1] Gazz. chim. ital., **24**, II, 469 (1894).
[2] *Ibid.*, **25**, II, 25 (1895).
[3] Ber. d. chem. Ges., **28**, 362.
[4] *Ibid.*, **42**, 2836 (1909).
[5] *Ibid.*, **42**, 3542 (1909).



He states that the compound is colorless, but becomes intensely red when treated with soda solution.

From this brief review of the literature it will be seen that it is not possible to say whether the group $>C=NOH$, *when present in a five-membered ring*, acts as a chromophore or not. Further study of phthaloxime was therefore undertaken and it was soon found that it could be obtained in two modifications, one *colorless* and the other *colored*.

EXPERIMENTAL

Phthaloxime (Colorless)

This phthaloxime was made according to the method of Lach from 220 grams of pure phthalic anhydride, 130 grams of hydroxylamine hydrochloride, 99 grams of sodium carbonate and 500 cc. of water. The mixture was heated in a water bath to 60° for about an hour, allowed to cool, and the *colorless* crystals filtered off, dried and weighed. The yield was about 70 per cent. The product was recrystallized from ethyl alcohol, some hydrochloric acid being added to the solution just before removing it from the water bath. This was for the purpose of decomposing any sodium or hydroxylamine salt of the phthaloxime which may have been present. The substance crystallizes in long *colorless* needles, easily soluble in hot alcohol or acetone, only slightly in the cold. It is also soluble in hot water, but much less so than in alcohol or acetone. In benzene and in ether the crystals are insoluble, but they dissolve quite readily in hot glacial acetic acid. In all cases in which the colorless substance dissolves in solvents containing a hydroxyl group, especially if the solution be heated, it was noted that the solution becomes *yellow*, owing to the formation of some of the colored isomer. Analyses,

by the Kjeldahl method, of the product recrystallized from alcohol and dried to constant weight at 100° after first reducing the substance with zinc dust, gave the following results:[1]

Substance Gram	Tenth-normal hydrochloric acid cc.	Nitrogen Per cent.
0.2668	16.29	8.55
0.2067	12.70	8.61
Calculated for $C_6H_4\begin{smallmatrix}C{=}NOH\\ \diagup\quad\diagdown O\\ C{=}O\end{smallmatrix}$		8.59

From these results it seemed quite certain that the product was phthaloxime. As it was *absolutely without color*, while both Lassar-Cohn and Errera describe their product as faintly *yellow*, complete combustion analyses were made of the substance.

(1) 0.1928 gram substance gave 0.4157 gram CO_2 and 0.0579 gram H_2O.

(2) 0.3450 gram substance gave 0.7426 gram CO_2 and 0.0950 gram H_2O.

(3) 0.2113 gram substance gave 16.35 cc. N at 20°; bar., 739.8 at 19°.5.

(4) 0.2505 gram substance gave 19.00 cc. N at 18°.4; bar., 748.7 at 20°.3.

	Carbon Per cent.	Hydrogen Per cent.	Nitrogen[2] Per cent.
Found	(1) 58.80	3.33	(3) 8.54
	(2) 58.70	3.08	(4) 8.54
Calculated for $C_6H_4\begin{smallmatrix}C{=}NOH\\ \diagup\quad\diagdown O\\ C{=}O\end{smallmatrix}$	58.88	3.09	8.59

There can be no doubt, from these analyses, that the product is phthaloxime. It melts with decomposition when quickly heated in a sealed tube at 220°–226°, uncorr. (a thermometer standardized by the Physikalisch-Technische Reichsanstalt was used), and turns red at once in contact with ammonia,

[1] International atomic weights for 1911 are used in all calculations in this paper.

[2] The barometer used in all our determinations had a *brass* scale. See also THIS JOURNAL, 44, 11, footnote 5.

forming the red ammonium salt. It crystallizes from water without water of crystallization, as the air-dried product loses no weight when heated to 110°. Long-continued heating at this temperature decomposes the substance and some phthalic anhydride sublimes. Like the faintly *yellow* phthaloxime of Lassar-Cohn, it gives red potassium, sodium and silver salts. Crystals from alcohol were examined by Professor Gill, of the Mineralogical Department, who describes them as follows:

Phthaloxime (*Colorless*).—The crystals are monoclinic needles elongated in the direction of the *b* axis and usually flattened parallel to a pair of faces in the ortho-zone. They are so much striated and so frequently bent that accurate measurements were not found possible. The determination of the system of crystallization rests upon the parallel extinction in all positions when the needle is laid horizontally on the stage of the polarizing microscope and rotated about its long diameter, and on the angles of this principal zone, which were found, by taking the best measurements of some fifteen or twenty crystals, to be 64° 54′, 44° 55′, 29° 59′ and 40° 11′. These angles are probably correct to within 5′. End faces could be measured on only two crystals giving angles of 71° 20′ with those faces in the zone of elongation which makes angles of 64° 54′ and 44° 55′ with their adjacent forms. The pair of end faces intersect at right angles to the axis of the needles. The substance has such a peculiar fibrous texture that cross sections of the needles could not be broken off for optical study. The double refraction is extremely high, several determinations giving results of about 0.300. A rough measurement of the index of refraction for yellow light vibrating parallel to the elongation of the crystals (greatest elasticity) gave 1.522.

Phthaloxime (*Yellow*)

This product was first obtained from the aqueous mother liquor from which two crops of the *colorless* phthaloxime had already separated, one on cooling and the other on standing overnight. On heating this mother liquor in a boiling water bath for about one and a half hours

and allowing the solution to cool, a considerable amount of long *lemon-yellow needles* crystallized out. These were at first thought to be a hydroxylamine salt of the phthaloxime, as a 25 per cent. excess of hydroxylamine had been used in making the phthaloxime. When recrystallized, however, from water or alcohol containing hydrochloric acid the same lemon-yellow needles were obtained and *not* the *colorless* phthaloxime already described. Further investigation soon showed that this yellow substance is an isomer of the *colorless* phthaloxime, and that it could be obtained *exclusively* by using the same proportions of materials as in making the white product, but heating the mixture in a beaker surrounded with boiling water for three-quarters of an hour or more. On cooling, the yellow crystals were filtered off and recrystallized from alcohol containing hydrochloric acid. The yield was about 60–70 per cent. Analyses by the Kjeldahl method, after reduction with zinc dust, gave the following results on the product dried at 100°:

Substance Gram	Tenth-normal hydrochloric acid cc.	Nitrogen Per cent.
0.1306	8.02	8.60
0.2203	13.56	8.62
0.2088	12.84	8.62
Calculated for $C_6H_4\begin{matrix}C{=}NOH\\ \diagup\quad\diagdown O\\ C{=}O\end{matrix}$		8.59

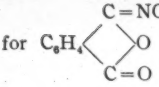
Complete combustion analyses gave the following results:

(1) 0.2010 gram substance gave 0.4356 gram CO_2 and 0.0573 gram H_2O.

(2) 0.2748 gram substance gave 0.5952 gram CO_2 and 0.0776 gram H_2O.

(3) 0.3174 gram substance gave 24.65 cc. N at 18°; bar., 739.7 mm. at 23°.3.

(4) 0.2861 gram substance gave 22.13 cc. N at 19°.5; bar., 739.8 mm. at 23°.3.

		Carbon Per cent.	Hydrogen Per cent.	Nitrogen Per cent.
Found		(1) 59.10	3.16	(3) 8.65
		(2) 59.07	3.14	(4) 8.55
Calculated for		58.88	3.09	8.59

The yellow crystals therefore have the same percentage composition as the white product and there are hence two phthaloximes, one *colorless* and the other *colored*. Both products melt with decomposition at approximately the same temperature, when heated rapidly in sealed capillary tubes, and a mixture of the two oximes melts at the same temperature (220°–226°). Neither contains water or alcohol of crystallization and both are decomposed on long continued heating at 110°, when some phthalic anhydride sublimes. Neither oxime forms a hydrochloride when treated with dry hydrochloric acid gas, either in the solid state or in solution. In this respect they differ very markedly from the benzaldoximes. Both oximes dissolve in caustic alkalis with a red color and when these solutions are allowed to stand or are heated gently they soon become colorless, owing to the formation of the salts of the hydroxamic acid. This may be shown by acidifying the dilute alkaline solution and adding ferric chloride solution, when the purple color characteristic of the hydroxamic acids appears.

Both form red ammonium, potassium, sodium and silver salts, which are isomeric and not identical, for the original substance is regenerated from these salts when they are decomposed by acids, i. e., the yellow product gives a red ammonium salt, and when this is treated with acid the yellow phthaloxime is regenerated, and the white product acts the same way, regenerating the white phthaloxime. The white oxime gives a *white* ether and the yellow oxime a *yellow* ether when their silver salts react with ethyl iodode in the *cold*, and two acetates, one *white* and the other *yellow*, have also been obtained, one from the white and the other from the yellow oxime.

Crystals of the yellow product from alcohol were examined by Professor Gill, who reports as follows:

Phthaloxime (*Yellow*).—No definite distinction in the shape of optical properties could be established between this substance and the white form, except its yellow color. This color seems due largely to fluorescence, though it may be a manifestation of absorption dependent on the fibrous character of its crystals. Only one of the three axes of elasticity shows absorption enough to exhibit pleochroism. This is nearly normal to the larger faces of the flattened needle, so that the color is seen when they are viewed on edge in light vibrating transversely.

The value 1.529 found for the index of refraction of yellow light vibrating parallel to the length of the crystals is not distinctive, since the prism angles could not be very accurately determined, and the setting for least deviation was made only approximately (on the yellow part of the spectrum). On the whole, the yellow crystals seem a little clearer and better crystallized than the white, also somewhat less flattened, and more constant in being flattened parallel to the same pair of faces of the zone of elongation. These differences, however, may well be due to slight differences in the conditions of crystallization.

One very interesting fact in connection with the yellow phthaloxime is that the substance, although it appears to have a marked yellow color, really owes all, or at least most, of its color to *fluorescence*. In this the product resembles in some respects potassium uranyl sulphate, which in the solid form has, to the unaided eye, a somewhat similar *yellow fluorescence*. It is evident that, as Lassar-Cohn and Errera both describe their product as having a faint yellow color, they had a mixture of the *colorless* and the *colored* phthaloximes. The derivatives, also, which they made were probably mixtures. It was therefore thought to be desirable to make and study the derivatives of the *colorless* and *colored* phthaloximes and see if any explanation of this peculiar isomerism could be found. Investigation soon showed that the white product could be converted quantitatively into the yellow

isomer by simply boiling its solution in glacial acetic acid for about one hour. This process is similar to the conversion of the aldoximes into their stereoisomers. On cooling, the yellow product crystallizes out, especially if some water be added to the solution. This transformation of the colorless into the colored product takes place to some extent whenever the white substance is dissolved in any solvent containing a hydroxyl group and the solution heated, and explains the statement of Lassar-Cohn that after repeated crystallization phthaloxime has a faint yellow color.

The change of the white into the yellow oxime is connected in some way with the hydroxyl group, for it takes place to some extent in boiling methyl alcohol, water, ethyl alcohol and most readily in glacial acetic acid. The change is not due to temperature alone, however, for the white is not converted into the yellow oxime by simply heating it in the solid state nor by boiling its solution in xylene for two or more hours, even in the presence of a small amount of glacial acetic acid. The white and the yellow oximes undergo no change when boiled with xylene, but crystallize from the solution in the original form. Repeated crystallization of the yellow product from alcohol did not increase its color, hence it probably contained very little, if any, of the white oxime. A mixture of the two oximes crystallizes out as a faintly yellow product and the slightest trace of the yellow oxime can be detected in the white compound by the faint yellow color shown by the crystals *after they have been filtered from the solution.*

Neither oxime undergoes any change in the sunlight. A quartz tube containing samples of both oximes has been exposed to the light since May 1, 1911, but no change has taken place. The colorless oxime therefore differs from that of Meyer obtained from hydroxydiphenylphthalide. According to Meyer, the colorless oxime of hydroxydiphenylphthalide becomes colored on standing in the light.

The reverse transformation of the yellow into the white isomer can also be brought about *quantitatively* by *boiling* the yellow product with acetic anhydride, when the same colorless acetate results as is obtained when the white phthal-

oxime is acetylated. When this colorless acetate is saponified in the cold with ammonia solution and an acid added, the white phthaloxime is precipitated. A *yellow* acetate was obtained from the yellow oxime by acetylating with acetic anhydride at *room temperature*. Attempts to reduce the oximes with hydriodic acid and with zinc dust and hydrochloric acid gave phthalic acid, identified by the formation of fluorescein when heated with resorcinol. As was to be expected, the white and yellow oximes show a difference in the amount of light absorbed, as is seen in the accompanying photograph of the absorption spectra. The Nernst light control is at the lower part of the photograph, below the lower scale. Just above this scale are two spectra of the white oxime, and above these two of the yellow isomer. In both cases it will be seen that the yellow absorbs more light than the white oxime, all the violet end of the spectrum nearly to the green being cut off; while the white oxime transmits nearly all of the visible spectrum and only cuts off the extreme violet. The photograph was made with a Hilger spectrograph, a Schwann lamp with Nernst glower being used. All prisms and lenses used were of quartz and the oxime solutions, which were two per cent. solutions in absolute ethyl alcohol, were contained in very thin Jena-glass vessels. The thickness of the solutions was 4 cm. and Cramer's special spectrum plates were used in making the negative.

Salts of the Two Phthaloximes

Ammonium Salt of the White Oxime.—Ammonia gas dried by means of soda-lime was passed over a weighed amount of the *white product*, contained in a platinum boat, until constant weight was obtained. The results were as follows:

Substance Gram	Gain Gram	Gain Per cent.
0.2087	0.0218	10.45
0.3464	0.0363	10.47

Calculated for the formation of $C_6H_4 \begin{cases} C{=}NONH_4 \\ \\ C{=}O \end{cases} O$ 10.45

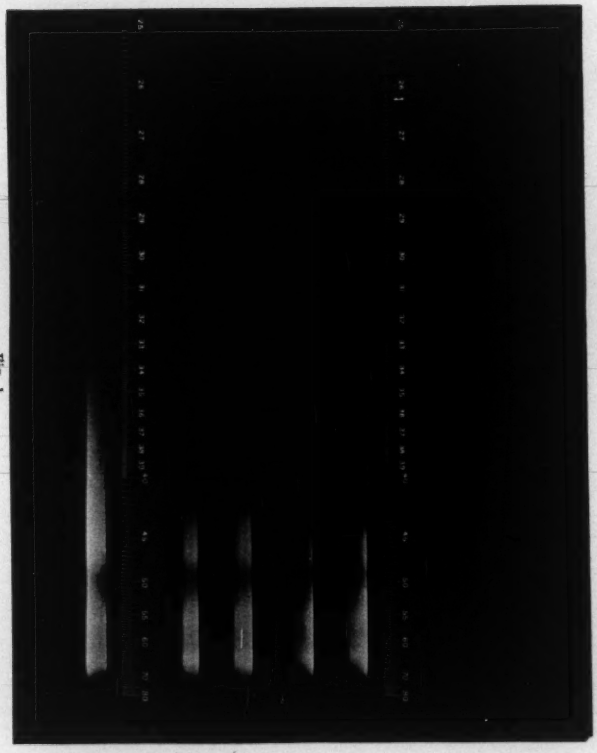


Fig. 1.

The *white* phthaloxime turns *red* at once as soon as the ammonia reaches the product. The ammonium salt loses ammonia slowly on standing in the air at ordinary temperatures. When heated to 110° it gives off the ammonia rapidly, leaving the *white* oxime. It is difficult to expel the last traces of ammonia, however, without decomposing some of the phthaloxime and driving off phthalic anhydride.

The ammonium salt was also made by dissolving the *white* oxime in alcohol and adding some aqueous ammonia. The precipitated ammonium salt was then recrystallized from alcohol and analyzed by dissolving a weighed quantity of the red crystals in water and titrating with tenth-normal hydrochloric acid until the solution was colorless.

Substance Gram	Tenth-normal hydrochloric acid cc.	Ammonia Per cent.
0.0534	2.94	9.38
0.0794	4.32	9.27
0.0363	1.99	9.35
Calculated for $C_6H_4\begin{cases}C{=}NONH_4\\ \\ CO\end{cases}O$		9.46

The ammonium salt dissolves in water with a red color and when an acid is added the *white* oxime precipitates.

Ammonium Salt of the Yellow Oxime.—This compound was made from the *yellow* oxime and ammonia gas by the method given above. Analyses:

Substance Gram	Gain Gram	Gain Per cent.
0.2095	0.0218	10.41
0.1636	0.0171	10.45
Calculated for the formation of $C_6H_4\begin{cases}C{=}NONH_4\\ \\ CO\end{cases}O$		10.45

The yellow oxime turns red immediately in contact with the ammonia and the product cannot be distinguished from the

ammonium salt of the white oxime in appearance or color. When heated to 110° the salt loses its ammonia, regenerating the *yellow* oxime. The ammonium salt was also made by the second method given above and titrated in the same way:

Substance Gram	Tenth-normal hydrochloric acid cc.	Ammonia Per cent.
0.0777	4.35	9.53
0.0900	5.03	9.52
Calculated for $C_5H_4\begin{cases} C{=}NONH_4 \\ \diagup\quad\diagdown O \\ CO \end{cases}$		9.46

This salt also dissolves in water with a red color, exactly like that given by the salt of the white oxime. When the solution is acidified, however, the *yellow* oxime is precipitated.

Professor Gill reports as follows regarding the crystallography of these two salts:

Ammonium Salt of the White Oxime.—The substance occurs in the form of extremely fine red needles, with no sharp end faces observable under the microscope. Extinction is parallel, double refraction rather low, and pleochroism strong. The ray vibrating parallel to the direction of elongation appears straw-yellow in color, while that vibrating transversely shows a deep reddish orange. The substance is probably orthorhombic.

Ammonium Salt of the Yellow Oxime.—This substance exhibits no differences from the salt of the white form, except such as would be explained by the somewhat smaller size of the needles, viz., less marked pleochroism, lower interference color, etc.

Sodium Salt of the White Oxime.—This salt was made by adding an alcoholic solution of sodium ethylate to an alcoholic solution of the white oxime. The precipitate which forms has a deep red color and is well crystallized. It is only slightly soluble in alcohol, but dissolves readily in cold water. When this solution is acidified the *white* oxime precipitates. Analyses by titration:

Substance Gram	Tenth-normal hydrochloric acid cc.	Sodium Per cent.
0.0385	2.11	12.60
0.0472	2.55	12.43
Calculated for $C_6H_4\begin{smallmatrix}C=NONa\\ \diagup\quad\diagdown\\ CO\end{smallmatrix}O$		12.43

The same red salt precipitates when an alcoholic solution of sodium acetate and the oxime is *boiled* for a few minutes, as shown by the following analyses:

Substance Gram	Tenth-normal hydrochloric acid cc.	Sodium Per cent.
0.0708	3.81	12.38
0.1070	5.75	12.36
Calculated for $C_6H_4\begin{smallmatrix}C=NONa\\ \diagup\quad\diagdown\\ CO\end{smallmatrix}O$		12.43

Sodium Salt of the Yellow Oxime.—This salt was made from the yellow oxime and sodium ethylate. It has the same color and appearance as the sodium salt from the white oxime, but gives the yellow oxime when its solution is acidified. Analyses:

Substance Gram	Tenth-normal hydrochloric acid cc.	Sodium Per cent.
0.1945	10.51	12.42
0.1678	9.09	12.45
Calculated for $C_6H_4\begin{smallmatrix}C=NONa\\ \diagup\quad\diagdown\\ CO\end{smallmatrix}O$		12.43

Professor Gill reports as follows regarding the crystallography of these two salts:

Sodium Salt of the Yellow Oxime.—This substance closely resembles the silver salt in color and crystallization. The glistening scales are aggregates of extremely small platy or spear-head shaped crystals, usually without sharp outlines. The interference colors are all of the first order, but the crys-

tals are so thin that this may not mean especially low double refraction. Pleochroism from pale to much deeper purplish-red is rather marked. Extinction appears to be about parallel, and the plates show a symmetrical, but much blurred, interference figure. Hence the crystal form seems to be orthorhombic.

Sodium Salt of the White Oxime.—This substance shows only slight difference in crystal habitus from the foregoing, occurring in more elongated forms. Otherwise its properties are the same.

Acid Sodium Salt of the White Oxime.—This salt is obtained by cautiously adding an alcoholic solution of sodium acetate to a solution of the *white* oxime in alcohol until a small amount of the above red salt separates. This is then filtered off and the filtrate allowed to stand. Orange crystals of the acid salt then slowly form. These may be obtained in fairly large crystals, although a partial change into the *red* salt always takes place at the surface of the liquid.

The orange salt cannot be recrystallized, as heating even with absolute alcohol causes a complete change into the red salt. Hence, in making the acid salt the liquid must not be heated. It is not very soluble in cold water and dissolves with decomposition, as is shown by the separation of some of the white oxime.

It dissolves completely in hot water, because this dissolves both the salt and the oxime. It is readily soluble in sodium hydroxide solution, forming the red sodium salt. When solutions of the acid salt are acidified the white oxime is precipitated. Analyses:

Substance Gram	Tenth-normal hydrochloric acid cc.	Sodium Per cent.
0.0717	2.03	6.52
0.1271	3.64	6.59
Calculated for $C_6H_4\langle^{C=NONa}_{CO}\rangle O + C_6H_4\langle^{C=NOH}_{CO}\rangle O$		6.61

0.3393 gram substance gave 25.3 cc. N at 27°; bar., 743.5 at 22°.

	Nitrogen Per cent.
Found	7.97
Calculated for $C_6H_4\langle \overset{C=NONa}{CO} \rangle O + C_6H_4\langle \overset{C=NOH}{CO} \rangle O$	8.04

Acid Sodium Salt of the Yellow Oxime.—Analyses of this salt, which was made in the same way as the corresponding salt of the *white* oxime, gave the following results:

Substance Gram	Tenth-normal hydrochloric acid cc.	Sodium Per cent.
0.0774	2.23	6.63
0.0867	2.46	6.53
Calculated for $C_6H_4\langle \overset{C=NONa}{CO} \rangle O + C_6H_4\langle \overset{C=NOH}{CO} \rangle O$		6.61

0.3104 gram substance gave 23.35 cc. N at 27°.3; bar., 741.3 mm. at 22°.

	Nitrogen Per cent.
Found	8.00
Calculated	8.04

This sodium salt gives the *yellow oxime* when its solution is acidified.

Professor Gill reports as follows concerning the crystallography of these two salts:

Acid Sodium Salt from the White Oxime.—The small orange-yellow crystals are stout columnar to long acicular in habitus. The needles show rather strong double refraction, well marked pleochroism from greenish yellow to orange-yellow, and an extinction angle of 8° to 20°, mostly 10° to 12°. One crystal was found large enough to give faint reflections on the goniometer. The angles of the three pairs of faces in the zone of elongation were about 54°, 76°.5 and 49°.5. These angles, taken together with the oblique extinction, prove the substance to be triclinic.

Acid Sodium Salt from the Yellow Oxime.—The substance is

crystallographically indistinguishable from that derived from the white oxime. The extinction angle is 6° to 20°. No measurements could be made on the goniometer, but a needle set on end under the microscope showed a prism angle of approximately 76°.

Acid Potassium Salt of the White Oxime.—When concentrated alcoholic solutions of the *white* oxime and potassium acetate were brought together a spongy, slimy, light orange material resembling bunches of sea-weed was thrown down. This product is difficultly soluble in alcohol and attempts to crystallize it from this solvent gave the same slimy material.

If *warm* and *dilute* alcoholic solutions of the oxime and potassium acetate are used the acid salt is precipitated in the form of reddish flakes which have a beautiful golden yellow luster. These were washed with alcohol, dried and analyzed:

Substance Gram	Tenth-normal hydrochloric acid cc.	Potassium Per cent.
0.0717	1.93	10.52
0.1155	3.11	10.52
0.2106 gram gave 0.0495 gram K_2SO_4		10.55
Calculated for $C_6H_4\langle\begin{smallmatrix}C{=}NOK\\ \\ CO\end{smallmatrix}\rangle O + C_6H_4\langle\begin{smallmatrix}C{=}NOH\\ \\ CO\end{smallmatrix}\rangle O$		10.73

0.3476 gram substance gave 24.2 cc. N at 15°.4; bar., 758 mm. at 22°.

0.1755 gram substance gave 12.85 cc. N at 17°.5; bar., 738.8 mm. at 23°.3.

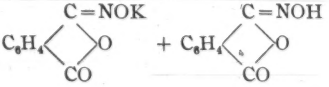
	Nitrogen Per cent.
Found	8.06
	8.16
Calculated for $C_6H_4\langle\begin{smallmatrix}C{=}NOK\\ \\ CO\end{smallmatrix}\rangle O + C_6H_4\langle\begin{smallmatrix}C{=}NOH\\ \\ CO\end{smallmatrix}\rangle O$	7.69

It is difficult to obtain the salt perfectly pure, as it cannot be recrystallized. It differs markedly from the corresponding sodium salt in that boiling with alcohol, even in the presence

of potassium acetate, does not change it to the red potassium salt. Indeed, this acid potassium salt is the only one formed when potassium acetate is used. It is not very soluble in cold water and is decomposed partially into the white oxime and its potassium salt by water, as is shown by the separation of white particles of the oxime. It dissolves readily in caustic potash solution, forming the red potassium salt. When the solutions of the acid salt are acidified the white oxime is precipitated.

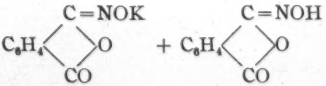
Acid Potassium Salt of the Yellow Oxime.—This salt was made by the method given above for the corresponding salt of the white oxime, which it resembles very closely both in appearance and in properties. When the solution of the salt is acidified the *yellow* oxime is precipitated. Analyses:

Substance Gram	Tenth-normal hydrochloric acid cc.	Potassium Per cent.
0.0628	1.70	10.58
0.0511	1.43	10.94
0.0756	2.05	10.60

Calculated for  10.73

0.2911 gram gave 21.65 cc. N at 21°.5; bar., 745.3 mm. at 21°.5.

	Nitrogen Per cent.
Found	8.18

Calculated for  7.69

The crystals of the two salts are described by Professor Gill as follows:

Acid Potassium Salt from Yellow Oxime.—The large macroscopic flakes are seen under the microscope to be made up of innumerable thin, sharply bounded flat crystals. These are too small to give interference figures in converged polarized light. They are six-sided (or rarely square) in shape. This

variation in outline is due to the greater or less development, or even absence, of one pair of the bounding faces. Extinction is parallel to this pair of faces, and symmetrical to the other two pairs, which make angles of nearly 90° with each other. It is highly probable, therefore, that the crystallization is orthorhombic, with two of the axes nearly equal in length. The double refraction is rather strong, since these very thin plates produce interference colors of the second order. Pleochroism is marked, the ray vibrating normal to the variable-sized (pinacoid) faces being pale yellow, and that parallel to them orange.

Acid Potassium Salt from White Oxime.—The only difference from the salt of the yellow form that was noted is the somewhat more frequent occurrence of square shapes. This is very likely due to slightly different conditions of crystallization.

Silver Salt of the White Oxime.—When aqueous solutions of the sodium salt of the white oxime and silver nitrate are mixed the silver salt is precipitated as a deep red, gelatinous mass. When this is filtered off, washed with water and suspended in alcohol it becomes beautifully crystalline, forming tiny red flakes. It was washed several times with alcohol, then with ether and dried in the water oven. It was analyzed by dissolving in hot concentrated nitric acid, diluting with water and titrating with tenth-normal ammonium sulphocyanate, ammonium ferric sulphate being used as the indicator.

Substance Gram	Tenth-normal ammonium sulphocyanate cc.	Silver Per cent.
0.1315	4.88	40.02
0.2081	7.72	40.00
Calculated for $C_6H_4\begin{cases} C=NOAg \\ CO \end{cases}O$		39.97

Silver Salt of the Yellow Oxime.—This salt was made and purified in the same way as the silver salt of the white oxime.

Analyses:

Substance Gram	Tenth-normal ammonium sulphocyanate cc.	Silver Per cent.
0.1718	6.36	39.93
0.2551	9.44	39.92
Calculated for $C_6H_4\begin{cases}C=NOAg\\ \\ CO\end{cases}O$		39.97

When these silver salts are decomposed by nitric acid the *oxime from which the salt was made* is regenerated.

The crystals of the two silver salts are described by Professor Gill as follows:

Silver Salt of the Yellow Oxime.—The crystals occur in the form of minute red plates or scales with rather irregular outline. Wherever approximately rectilinear boundaries are present, extinction appears to be either parallel or at an angle of about 45°. The optical figure in converged polarized light is not distinct, but suggests an obtuse bisectrix or optical normal in the center of the microscope field. Like the acid potassium salt, therefore, it is probably *orthorhombic*, with a prism angle of nearly 90°.

The double refraction is rather low, only first order grays being observable as interference colors on the extremely thin plates. Pleochroism from a purplish red to a brick-red is rather weak, but distinct.

Silver Salt of the White Oxime.—This substance is indistinguishable from the corresponding salt of the yellow form. Considering the flat face as the base, one crystal showed a prism angle of 96°, as measured by the cross hairs of the microscope, and apparently the brachy-pinacoid. The brick-red color is shown by light vibrating parallel to the brachy-axis, which is an axis of less optical elasticity than the macro-axis.

Acetate of the White Oxime.—This product results when the *white* or *yellow* oxime is *boiled* with an excess of acetic anhydride for half an hour. On cooling, the mixture is poured into water, and the crystals filtered off and recrystallized from alcohol and from benzene. Yield, 97.5 per cent. Melting point,

183°–185° (uncorr.). Product colorless and crystallizes beautifully in monoclinic prisms. Analyses of the product from the white oxime:

0.3056 gram substance gave 18.8 cc. N at 15°.3; bar., 746.7 at 19°.8.

0.3157 gram substance gave 18.9 cc. N at 18°.7; bar., 746.8 at 20°.

0.4095 gram substance gave 24.2 cc. N at 18°; bar., 758.1 at 20°.

	Nitrogen		
	Per cent.	Per cent.	Per cent.
Found	7.00	6.71	6.76
Calculated for $C_6H_4\begin{cases} C=NOCOCH_3 \\ O \\ CO \end{cases}$		6.83	

From the *yellow* oxime a *white* acetate was obtained identical with the above in melting point and crystal form and which on saponification gave the *white* oxime. This forms a convenient and quantitative method of converting the *yellow* into the *white* oxime. Analysis:

0.4189 gram substance gave 25.05 cc. N at 18°; bar., 754 mm. at 23°.3.

	Nitrogen Per cent.
Found	6.79
Calculated for $C_6H_4\begin{cases} C=NOCOCH_3 \\ O \\ CO \end{cases}$	6.83

The actate is very easily saponified in the cold. An alcoholic solution is hydrolyzed at once by aqueous caustic potash with the formation of salts of the hydroxamic and anthranilic acids. Alcoholic caustic potash or sodium ethylate produces a similar change, though less rapidly. The sodium salt of the white oxime may be readily obtained pure by adding the white acetate in the solid form to an alcoholic solution of sodium ethylate. The best method for the saponification of the acetate is to add a slight excess of ammonia to an alco-

holic solution of the acetate. The red ammonium salt at once separates. When this mixture is acidified the white oxime precipitates.

Acetate of the Yellow Oxime.—When the yellow oxime is treated with an excess of acetic anhydride and the mixture allowed to stand a few days at room temperature, it is completely transformed into a pale yellow acetate. Fairly large crystals may be obtained by recrystallization from benzene. These show a very decided yellow color. The melting point, 183°–185° (uncorr.), is the same as that of the white acetate and a mixture of the two acetates melts at the same temperature. Analysis:

0.4042 gram substance gave 25.55 cc. N at 24°; bar., 723.3 mm. at 21°.3.

	Nitrogen Per cent.
Found	6.77
Calculated for $C_6H_4\begin{cases} C{=}NOCOCH_3 \\ O \\ CO \end{cases}$	6.83

When saponified with ammonia, according to the method given under the white acetate, this yellow acetate always gives the yellow oxime. This fact and the color of the product show that it is not identical with the white acetate, notwithstanding that both have the same melting point.

Professor Gill reports as follows concerning the crystals of the two acetates from benzene:

Phthaloxime Acetate

Colorless Form.—Brilliant clear crystals 2 to 5 mm. in diameter were measured by Mr. F. A. Strauss, a student in Cornell University, who found them practically identical in form with the crystals measured by La Valle,[1] as follows:

Monoclinic, B = 85° 47½″, $a : b : c$ = 1.973 : 1 : 1.111. Forms observed: c = (001), a = (100), m = (110), n = (210), z = (011), x = (1$\bar{1}$1) and X = (11$\bar{1}$). The ordinary habitus is shown by the accompanying drawing.

[1] Gazz. chim. ital., **25**, II, 24.

Table of Angles

	Found	Calculated	(Calculated, La Valle)
100 : 001	*85° 47½′	.....	*85° 48′
110 : 100	63° 6′	63° 6½′	*63° 7′
110 : $\bar{1}$10	*53° 47′	.....	....
100 : 210	44° 50′	44° 32′	44° 36′
$\bar{1}$10 : 001	91° 52′	91° 54′	....
011 : 001	47° 53′	47° 56½′	*47° 55′
110 : 111	*38° 8′	.....	38° 6′
$\bar{1}\bar{1}$0 : $\bar{1}$11	39° 41½′	39° 44½′	....
111 : 001	50° 0′	49° 58′	50° 0′
$\bar{1}$11 : 001	52° 10½′	52° 9½′	52° 18′

The monoclinic symmetry is confirmed by the parallel extinction as seen on the base and on the orthopinacoid. Double refraction is very strong. The substance is negative, with a large optical angle and weak dispersion, blue > red. The plane of the optical axes was not determined as the figure was seen only in fragments of unknown orientation.

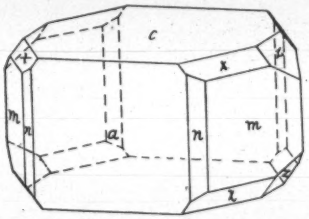


Fig. 2.

Yellow Form.—The crystals are pale yellow in color and transparent. Their crystal habitus is more varied than that of the colorless form, frequently occurring in flattened or elongated shapes. The angles seem to be identical with those of the colorless variety, but on four of the seven crystals examined the clino-domes at one end of the vertical axis were absent. This may indicate monoclinic-domatic symmetry, or the failure of these faces to appear may have been due to external causes.

These crystals show a distinct pleochroism, the ray vibrating parallel to the *b*-axis being colorless, while one or both of the

rays normal to this show an undoubted yellowish color. The optical behavior is otherwise exactly similar to that of the colorless compound.

The Ethyl Ether of the White Oxime.—The ethyl ether is *not* formed even on long continued boiling of the solution of the sodium salt in absolute alcohol with ethyl iodide. The reaction proceeds smoothly and quantitatively in the *cold* when the silver salt is used. The deep red gelatinous silver salt is made by the method already given, filtered and washed with suction and added while still moist to an ethereal solution of ethyl iodide. The mixture is allowed to stand in the dark at room temperature. In a few hours the red color disappears, the silver salt being completely converted into silver iodide. The ethereal solution of the ethyl ether is filtered off and the ethyl ether remaining in the silver iodide extracted with ether. The filtrates are combined, part of the ether distilled off and petroleum ether added to the hot solution until a slight turbidity results, a little ether is then added, and the solution filtered and allowed to cool slowly. The ethyl ether crystallizes in beautiful *colorless* prisms, melting at 95°–100° (uncorr.). Analyses:

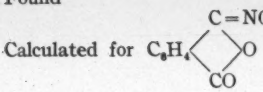
0.3611 gram substance gave 24.05 cc. N at 21.°5; bar., 732.7 mm. at 20°.5.

0.2965 gram substance gave 20.5 cc. N at 22°.5; bar., 732.3 mm. at 22°.6.

	Nitrogen		
	Per cent.	Per cent.	Per cent.
Found	7.23		7.46
Calculated for $C_6H_4\begin{cases} C=NOC_2H_5 \\ O \\ CO \end{cases}$	7.33		

The Ethyl Ether of the Yellow Oxime.—This ether was made from the silver salt of the *yellow* oxime by the method given above. The crystals have a *lemon-yellow color*, but melt at 95°–100° (uncorr.) and a mixture of the two ethers melts at the same temperature. Analysis:

0.3318 gram substance gave 22.85 cc. N at 22°; bar., 732 mm. at 22°.

	Nitrogen Per cent.
Found	7·44
Calculated for 	7·33

The ethers do not turn red when treated with solutions of the caustic alkalis as the oximes do, but dissolve very slowly on standing to form *colorless* solutions of phthalate and ethylhydroxylamine.

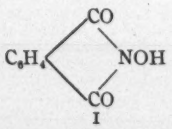
Professor Gill describes the crystals of the two ethers as follows:

Phthaloxime Ethyl Ether (*Colorless*). *Orthorhombic.*—Both the yellow and the white forms agree with determinations of shape and optical behavior made by Sommerfeldt[1] except that the unit pyramid (111) was not observed, while (221) was always well developed. It may be added that a good basal cleavage is present, so that plates are readily broken from the crystals, showing an acute bisectrix in converged polarized light, with an optical angle roughly estimated at 70°.

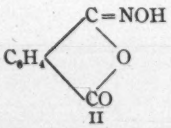
Phthaloxime Ethyl Ether (*Colored*).—The ether of the *yellow form* shows pleochroism, with a distinct greenish yellow tinge for the ray vibrating parallel to the macro-axis, while the other two elasticity-axes transmit colorless light.

THEORETICAL

Two explanations of this peculiar isomerism of the phthaloximes may be offered. The *colorless* isomer may be assumed to have the symmetrical (I) and the *colorless* compound the unsymmetrical (II) structure,



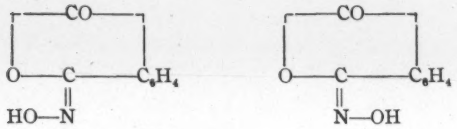
I



II

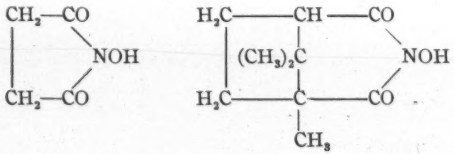
or both may be regarded as stereoisomers,

[1] Königsb. Diss., 7, 41 (1897–1898).



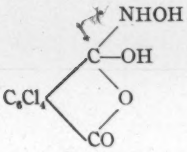
having the same structural formula (II).

The symmetrical formula has been almost invariably assigned to the *colorless* oximes, whether they form colored salts or not, by chemists working in this field. Thus Errera gives the symmetrical structure to succinyl- and camphorylhydroxylamines,

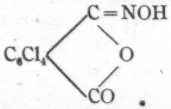


which are *colorless* and give *colorless* salts; Jaubert gives it to naphthaloxime, which he states is colorless, but forms colored salts; R. Meyer to the colorless oxime of hydroquinonephthalein and to the oximes of hydroxyphenylphthalide and hydroxydiphenylphthalide; and Villiger to dichlorophthaloxime, which, according to him, is colorless but becomes intensely red when treated with soda solution.

It is quite likely that the oxime of hydroxydiphenylphthalide made by R. Meyer also exists in two forms, *colorless* and *colored*, for he states that it was obtained as a *yellow* precipitate looking like phenolphthalein oxime, which crystallized from ether in *colorless* cubelike crystals but from alcohol in *yellow* crystals. Like the phthaloximes, both the colorless and the colored crystals have the same melting point. On recrystallizing the *yellow* product from ether, *colorless* crystals were obtained. Meyer also states that the colorless crystals become yellow on standing for some time in the air. Mr. E. H. Nichols has prepared tetrachlorophthaloxime from tetrachlorophthalic anhydride. A *colorless* addition product is first formed,

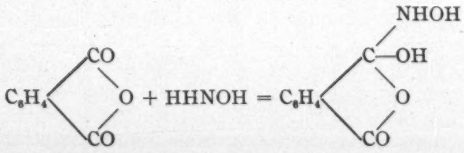


When heated this loses a molecule of water and gives the oxime,

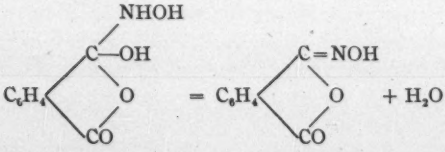


and the product then has a marked *yellow* color. Mr. Nichols has not yet succeeded in preparing the colorless tetrachlorophthaloxime, and it may be that it will not be possible to isolate it. This oxime also gives colored salts.

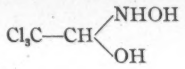
It seems highly improbable that the *colorless* phthaloxime has a different structural formula from its *colored* isomer, for both substances may be made from phthalyl chloride as well as from phthalic anhydride and hydroxylamine. Phthalyl chloride certainly has the unsymmetrical structure and therefore both oximes must have an analogous formula. Phthalic anhydride strikingly resembles *benzaldehyde* in a great many of its reactions, the *oxygen* of the *carbonyl* group acting exactly like the oxygen in the aldehyde group. It is highly probable, therefore, that the reaction between hydroxylamine and phthalic anhydride is to be represented as follows:



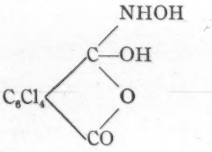
This then loses water, forming the oxime:



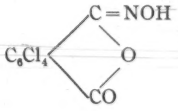
That the formation of the aldoximes proceeds in the same way is well known; indeed, in the case of chloral the addition product, chloralhydroxylamine,



has been isolated by Hantzsch.[1] It loses water even on standing in the air and goes over into the oxime. Mr. E. H. Nichols has found that tetrachlorophthalic anhydride acts in a similar manner to chloral, combining with hydroxylamine to form the compound



which, when heated, loses water and gives the colored oxime

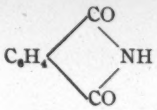


Another reason against assuming that the two phthaloximes are structural isomers is the ease with which they are converted into one another (see page 99). In this respect they resemble the benzaldoximes; indeed, they are more readily converted into each other than these substances. As is well known, stereoisomers are more readily transformed into each other than structural isomers. The great resemblance of benzaldehyde and phthalic anhydride to each other in their many reactions is also in favor of considering the phthaloximes as stereoisomers analogous to the two benzaldoximes.

Again, both phthaloximes form highly colored salts, whereas succinyl- and camphorylhydroxylamines, which are prob-

[1] Ber. d. chem. Ges., **25**, 702.

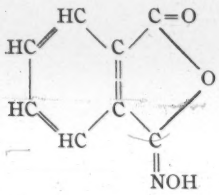
ably symmetrical, yield colorless salts, and the salts of phthalimide, which also has the symmetrical structure



are colorless.

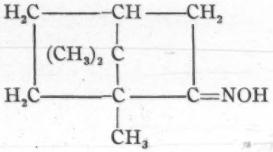
The remarkable resemblance crystallographically of the two oximes and their derivatives is also an argument in favor of identity in structure. The stereoisomerism of the phthaloximes, however, seems to be of a somewhat different character from that heretofore observed in the case of oximes, such as the benzaldoximes. Both phthaloximes and their acetates and ethyl ethers have the same melting points and no difference has been observed in the solubilities of the two isomers. Had one of the two substances not been *colored* it would have been impossible to detect the isomerism. As this color is largely due to the *fluorescence* of one of the isomers in the solid state, it may be said that the two products differ in their action on light. The isomerism bears a remarkable resemblance to that due to the presence of the asymmetric carbon or other atom. In this case also there is no difference in melting point or solubility of the dextro or levo product, the only difference being the way in which the two isomers act towards polarized light, and crystallographically. The two oximes, however, do not crystallize in hemihedral, enantiomorphous forms as is the case with optically active isomers, but they resemble each other remarkably closely in their crystallographic constants, much more closely, indeed, than would be expected were they merely structural isomers.

Perhaps the peculiar character of this stereoisomerism of the phthaloximes may be due to the fact that the oxime group is joined to a carbon atom which is present in a *five-membered ring:*

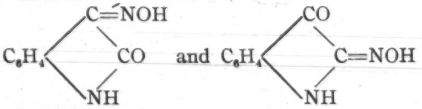


In none of the stereoisomeric oximes thus far investigated and recorded in the literature have the two groups attached to this carbon atom been contained in the same five-membered ring.

There is a similar grouping in the colorless camphoroxime,

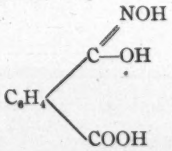


and in the two-colored oximes of isatine,



but stereoisomers of these substances have not been made as yet.

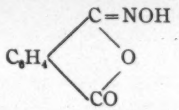
The effect of ring formation on the production of *color* is shown very well in the formation of the colored oxime from the colorless phthalhydroxamic acid,



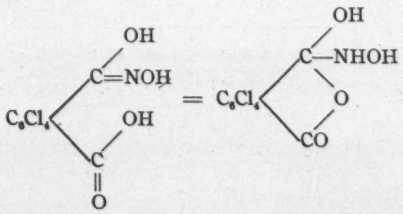
This substance, according to Lassar-Cohn,[1] is known only in solution, which has no color. It gives with ferric chloride the

[1] Ann. Chem. (Liebig), **205**, 307.

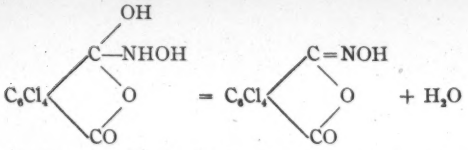
violet color so characteristic of the hydroxamic acids, and has a marked acid reaction. When its aqueous solution is heated to 100° it immediately becomes colored and on cooling the *yellow* oxime



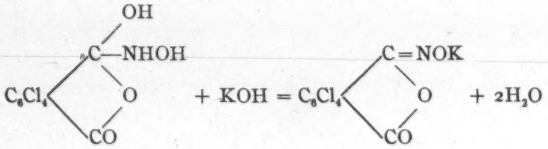
crystallizes out. This does not give the violet color with ferric chloride, but does give with alkalis the red color characteristic of the oxime and not given by the hydroxamic acid. Mr. E. H. Nichols has also found it impossible to isolate the tetrachlorophthalhydroxamic acid. When the *yellow* tetrachlorophthaloxime is treated with alkali it turns red and gradually dissolves, forming a *colorless* solution of the alkaline salt of the hydroxamic acid, for when this solution is diluted and acidified with hydrochloric acid and ferric chloride is added the *violet* color appears. When the colorless solution of the salt of the hydroxamic acid is acidified a *white* precipitate is formed which was at first thought to be the tetrachlorophthalhydroxamic acid. Investigation soon showed that its solution in dilute methyl alcohol did not give the *violet* color with ferric chloride, but that the solid material turned red immediately on contact with alkalis. It loses water when heated to 50° and even in a desiccator over phosphorus pentoxide at ordinary temperatures, and turns *yellow*, forming the oxime. This product is therefore isomeric with tetrachlorophthalhydroxamic acid, which is probably first formed and undergoes molecular rearrangement according to the equation



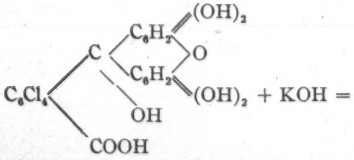
This product then loses a molecule of water, giving the yellow oxime:



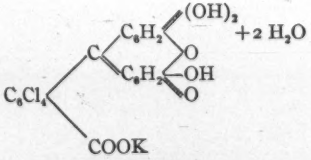
It is interesting to note that this loss of water can be brought about at ordinary temperatures and that it is accompanied by the *appearance of color*. The same reaction is brought about in the cold by alkalis, only here a *red* salt is formed:



This is somewhat analogous to the loss of water and formation of colored salts from a carbinol acid:[1]



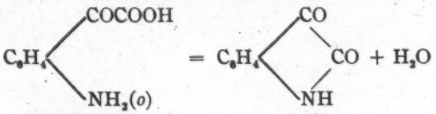
Tetrachlorgalleincarbinolcarboxylic Acid
(colorless)



Monopotassium Salt
(colored)

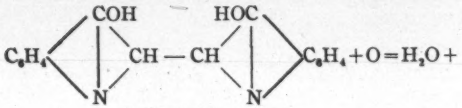
[1] THIS JOURNAL, **46**, 49

It seems therefore that the change into the *quinoid* condition in a *five-membered ring* can also bring about *color*. This is seen very well in the change of the colorless isatinic acid into isatine, even on standing in the air:

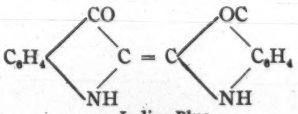


Isatinic Acid (colorless) — Isatine (red, quinoid)

and into the reddish violet alkaline salts of *isatine* in contact with alkalis. The transformation of indigo white into indigo blue by oxidation is also an instance of a similar character:



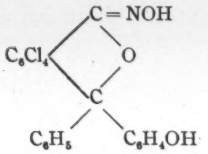
Indigo White



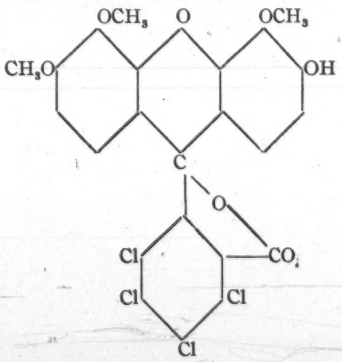
Indigo Blue (quinoid)

The formation of oximes similar to phthaloxime seems to be connected with the stability of the *five-membered ring*. Hjelt[1] found that phenolphthalein was more stable than diphenylphthalide and the latter more stable than phthalide itself. Now B. Lach states that phthalide *does not give an oxime*. The oxime of diphenylphthalide has not yet been made, but as R. Meyer has obtained the oximes of hydroxyphenylphthalide and of hydroxydiphenylphthalide and as we have prepared an oxime of hydroxydiphenyltetrachlorophthalide,

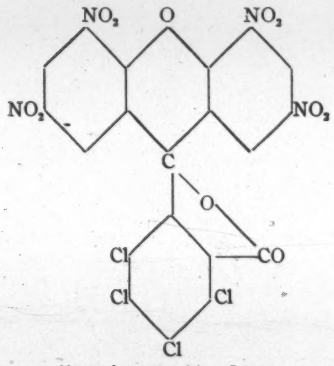
[1] Chem. Ztg., 18, 3 (1894).



which is *colored*, it seems highly probable that diphenylphthalide will also give an oxime. Finally, phenolphthalein, which Hjelt finds to contain the most stable ring of the three, yields an oxime with the greatest ease. Another fact, which also shows that the presence of a somewhat *stable five-membered ring* is essential for the oxime formation, is that fluorescein, which contains no such lactone ring, does not give an oxime according to Friedländer. We have found also that gallein and tetrachlorogallein do not give oximes, while the trimethyl ether of tetrachlorogallein,



which is *colorless* and resembles phenolphthalein very closely indeed, and does contain the five-membered lactone ring, gives a *red* oxime. Again, we have found that tetranitrotetrachlorofluoran,



Tetranitrotetrachlorofluoran

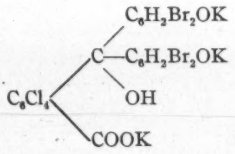
gives a *colored* oxime and hence there can be no doubt that the oximes of the phthaleins have the =NOH group attached to the carbon atom present in the *five-membered ring*, taking the place of the *carbonyl oxygen* atom.

It might be supposed, from what Friedländer[1] says, that when the phthaleins dissolve in alkali with a change in color they would react with hydroxylamine, for he states that the intensely blue to brown violet alkaline solutions of the *colorless* tetrabromophenolphthalein, of the *o*-cresolphthalein, hydroquinone-, pyrocatechol-, and orcinolphthaleins react very readily with hydroxylamine. The bright yellow solutions of the di- and tetranitrophenolphthaleins, however, do not. We have found also that phenoltetrachlorophthalein and tetraiodophenoltetrachlorophthalein, both of which are colorless and dissolve in alkalis with color, form oximes very readily, while tetrabromophenoltetrachlorophthalein, which is *colorless* and dissolves in alkalis with a *blue* color, acts like the dinitro- and tetranitrophenolphthaleins and does not form an oxime. This is perhaps due to the fact that the five-membered lactone ring is so easily broken in these compounds, owing to the acidifying influence of the halogens and the

[1] Ber. d. chem. Ges., **28**, 2259.

nitro groups. Tetrabromophenoltetrachlorophthalein, for example, combines in the cold with dry ammonia gas to form a *blue* diammonium salt, while phenolphthalein and phenoltetrachlorophthalein do not. This certainly indicates that the lactone ring is more easily broken in the tetrabromo compound.

Again, when the tetrabromo compound is dissolved in aqueous alkalis a comparatively slight excess of alkali renders its solution colorless, owing to the formation of the salt of the carbinol acid:



Now, as is well known, the formation of the oximes takes place best in the presence of an excess of alkali and this may be the explanation of the nonformation of the oxime in the case of the tetrabromophenoltetrachlorophthalein, for the addition of the excess of alkali to facilitate the oxime formation transforms the phthalein into the salt of the carbinol acid, which does not react with hydroxylamine. All the phthaleins which react with hydroxylamine to form oximes are *colorless*; that is, they have the *lactoid* structure and contain the lactone ring. None of the *colored* phthaleins, such as fluorescein, gallein, tetrachlorogallein or the di- and tetranitrophenolphthaleins, which have the *quinoid* structure, give oximes. This would certainly seem to show a very close connection between the lactone ring and the oxime formation.

CORNELL UNIVERSITY
ITHACA, N. Y.
October, 1911

THE ABSORPTION SPECTRA OF COMPARATIVELY RARE SALTS
THE SPECTROPHOTOGRAPHY OF CERTAIN CHEMICAL REACTIONS, AND THE EFFECT OF HIGH TEMPERATURES ON THE ABSORPTION SPECTRA OF NONAQUEOUS SOLUTIONS

By Harry C. Jones and W. W. Strong

[*Continued from the January number*]

Effect of Temperature on Absorption Spectra

The purpose of the work on absorption spectra at high temperatures was to obtain some knowledge, by means of changes produced in the absorption spectra, of the chemical changes that take place at these temperatures. The cells used have, in the main, been the quartz cell and the two steel cells described in the first part of this paper. Some qualitative observations were made with a hand spectroscope on solutions showing water and alcohol bands. The work done with the quartz cell was mainly with acid solutions, and this was done with a view to testing the stability of acid aggregates, as will be explained a little later. Some work was carried out on the change in the relative intensities of various solvate bands with change in temperature. This will also be taken up in detail.

The problem has been found to be a very difficult one, on account of trouble in closing the cell tightly, and very largely because of the formation of precipitates upon the windows of the cell.

Some work has been done dealing with the effects of pressure and high temperature upon solutions. W. N. Ipatieff[1] has shown that under a pressure of about 125 atmospheres of hydrogen, anthracene and phenanthrene were reduced, when heated in the presence of nickel oxide, to compounds such as $C_{14}H_{12}$, $C_{14}H_{14}$, $C_{14}H_{20}$, etc. From this work and that of others it has been shown that metals are precipitated from solutions of their salts by hydrogen under pressure. There appears

[1] Ber. d. chem. Ges., **41**, 966 (1908); **42**, 2078 (1909).

to be a critical temperature for the precipitation of each metal, silver and mercury being precipitated at ordinary temperatures under a pressure of 200 atmospheres from a decinormal solution, while copper and the more electropositive metals could not be precipitated even when the pressure exceeded 500 atmospheres. At 120° to 130°, however, branched crystals of copper were formed at 100 atmospheres; and at lower temperatures cuprous oxide was formed. Cobalt was precipitated at 180° to 200°, nickel at 200°, lead and bismuth at 240° to 250°, iron at 400° and 420 atmospheres. Ferric oxide was precipitated from an acetate solution at 350° and 230 atmospheres.

Among some of the investigators who have studied the effect of pressure and temperature on the conductivity of solutions are A. Bogojawlensky and G. Tammann in 1898, and F. Körber[1] in 1909. In most cases the resistance decreases as the pressure increases, but in many cases a minimum resistance is reached, after which a further increase in pressure will cause an increase in the resistance. This is true of solutions of potassium chloride at all temperatures between 0° and 100°. At 0° the minimum resistance is 0.872 of its original value, and is reached at 3000 kg. per sq. cm.; at 100° the minimum resistance ratio is 0.998 and this is reached at 900 kg. per sq. cm. Among halogen compounds the largest decrease of resistance is found for hydrogen chloride (17 per cent. for $V = 100$, $p = 3000$ and $t = 19°$) and lithium chloride (14 per cent.); and then follow potassium chloride (9), sodium chloride (8), potassium bromide (6), sodium bromide (5), potassium iodide (2) and sodium iodide (1).

Solvates and the Effect of Change in Temperature on the Relative Intensity of Solvate Bands

The absorption spectra of colored salts, in general, in the visible region are not very characteristic, but the absorption spectra of neodymium, erbium, uranyl, uranous and a few of the other rare-earth salts show fine characteristic bands, more or less distributed throughout the spectrum. There

[1] Z. physik. Chem., **67**, 212 (1909).

are, however, even among these spectra, very few cases where the absorption spectra of the same salt in different solvents, or of different salts of the same metal in the same solvent, are very different. There are, however, a few examples of well-defined "solvent bands," and some of these will now be discussed.

The most striking examples of the effect of the solvent on absorption spectra are those of water and ethyl alcohol upon several of the neodymium salts, water and alcohol upon uranous chloride or uranous bromide, and water and glycerol upon several uranyl and uranous salts. The spectra may well be described as consisting of the "water," the "methyl alcohol," the "glycerol," etc., bands of the particular salt. When the salt is dissolved in a mixture of two of the solvents, both sets of solvate bands appear, and if the solvents are mixed in a certain proportion, both sets of bands may be obtained of approximately the same intensity. The intensity of any set of solvate bands will be proportional to the amount of that solvent present. As the amount of the solvent present is changed, the solvate bands, in general, do not shift their position, but only change in intensity, and this change in intensity seems to be the same for all of the bands characteristic of that solvent. Solvent bands, in this respect, differ from the phosphorescent bands described by Lenard[1] and Klatt.

Just as a characteristic arc or spark spectrum has been regarded as indicating the presence of a certain element, just so a characteristic absorption spectrum will be regarded as evidence for the presence of a compound; and these compounds will be considered as being composed of one or more molecules or ions of the salt ("aggregate") and one or more molecules of the solvent. On account of the definite spectra, we shall speak of the "methyl alcoholate" of uranous chloride, the "hydrate" of neodymium bromide, etc.

Suppose, for instance, that the number of radicals in an aggregate of neodymium salt molecules and ions can vary,

[1] Ann. Physik. **31**, 642 (1910).

then the compound in which absorption takes place might be represented symbolically in the following manner:

$$x\{\overset{++}{UO_2}\}y\{UO_2Cl_2\}z\{\overline{Cl}\}a\{CH_3OH\}$$

and

$$x'\{\overset{+++}{Nd}\}y'\{NdCl_3\}z'\{\overline{Cl}\}a'\{CH_3OH\}$$

In most cases x, x', z and z' would probably be small; y and y' may also be small; and if hydrochloric acid or some other chloride is present, it might be possible to have systems of the following composition:

$$x_1\{\overset{++}{UO_2}\}x_2\{\overset{+}{H} \text{ or } \overset{++}{Ca}\ldots\}y_1\{UO_2Cl_2\}$$
$$y_2\{HCl,CaCl_2\ldots\}z\{\overline{Cl}\}a\{CH_3OH\}$$

$$x_1'\{\overset{+++}{Nd}\}x_2'\{\overset{+}{H},\overset{++}{Ca}\ldots\}y_1'\{NdCl_3\}$$
$$y_2'\{HCl,CaCl_2\ldots\}z'\{\overline{Cl}\}a'\{CH_3OH\}$$

The absorption may be due to some condition, possibly one of internal ionization, of the aggregate, and as long as the number of aggregates remains constant, Beer's law will hold. Free ions may split off from the aggregate without the character of the absorption being greatly changed. It might be that if the aggregates were completely broken up into their constituent ions and molecules, no characteristic absorption would be shown.

In this case, a and a' may either be considered as being constant, or as being so large that the atmosphere of the solvate around the absorber is so extensive that it is immaterial whether the outer solvent molecules are present or not. On account of the fact that solvent bands coexist, and do not shift into each other as the proportion of the solvents is changed, it will be assumed that at least the inner and effective solvent molecules are all of one kind in any "spectral" compound.

As to the numerical value of the y's, the absorption spectra, of course, do not furnish evidence. The phenomena of the constancy of the wave length of the uranyl sulphate and uranyl nitrate bands, with great dilution of these salts, lead to the conclusion that in this case, at least, the value of y is

greater than unity. Freezing-point, boiling-point, conductivity and osmotic-pressure measurements should aid in determining the values of x, y and z in the above equations.

The existence of complex aggregates of the above kind is quite rare in inorganic chemistry, although cases are known. Our own work on the reduction and oxidation of certain uranium salt and acid aggregates has shown that these different aggregates have very different chemical properties. Some cases of a series of a similar set of compounds might be cited, e. g., the cobaltammines. A large number of cobaltammines are known, and these have been divided into six series.

The diammine series, $[Co(NH_3)_2]X_4M$. In this series $X = NO_2$ and M is one atomic proportion of a monovalent metal, or the equivalent quantity of a divalent metal. These salts are prepared by the action of alkaline nitrites on cobaltous salts in the presence of a large amount of ammonium chloride or nitrate. The salts are yellow or brown crystalline solids, and are not very soluble in water.

The triammine series, $[Co(NH_3)_3]X_3$. X may be Cl, NO_3, NO_2, $^1/_2SO_4$, etc.

The tetrammine series, including

Praseo salts, $[R_2Co(NH_3)_4]X$. $X = Cl$.

Croceo salts, $[(NO_2)_2Co(NH_3)_4]X$.

Purpureo salts, $[RCo(NH_3)_4.H_2O]X_2$.

Roseo salts, $[Co(NH_3)_4(H_2O)_2]X_3$.

Fuseo salts, $[Co(NH_3)_4]OH.X_2$.

For the methods of preparation see O. Dammer's *Handbuch der anorganischen Chemie*, Vol. 3.

The pentammine purpureo salts, $[RCo(NH_3)_5]X_2$, where X may be Cl, Br, NO_3, NO_2, $^1/_2SO_4$, etc. The pentammine nitrito salts are known as the xanthocobalt salts, and have the general formula $[NO_2Co(NH_3)_5]X_2$. The pentammine roseo salts can be obtained by the action of concentrated acids in the cold on oxidized solutions of cobaltous salts. They are of a reddish color. On heating with concentrated acids they become purpureo salts.

The hexammine or luteo series has the composition $[Co(NH_3)_6]X_3$. These salts form yellow or bronze-colored

crystals which decompose on boiling. The above examples are cited because the cobalt salts give absorption band spectra in some cases similar to the uranyl bands. It is very probable that uranium, neodymium, erbium, etc., give rise to much more complex compounds than even cobalt.

It will be assumed that the absorption bands are due to compounds that represent the average condition of the given dissolved salt. It may be that only a few of the particles of the absorbing salt may be active at any one instant. For instance, Becquerel[1] considers that only a very small number of the neodymium atoms take part in the absorption of light at any moment. It may be that the absorption takes place only when the compound is in a special condition. For example, in the case of the uranyl salts we may think of the absorption as being due to the valency electrons in the UO_2 group. The absorption may take place when one of these electrons leaves the uranium or oxygen atoms, or when it returns. Whatever the mechanism may be, it will be assumed that the frequency of the absorber is determined by the nature of the compound in which it is located, and that this compound is typical of the average of all the possible compounds in the solution. Accordingly, if the "methyl alcohol" and "water" bands of uranous bromide dissolved in methyl alcohol and water are of approximately the same intensity, it follows that there are equal amounts of the uranous bromide existing as the "methyl alcoholate" and as the "hydrate."

In the case of neodymium chloride or neodymium bromide Jones and Anderson[2] have shown that the "water" and "alcohol" bands are of about equal intensity when the solvent consists of 8 per cent. of water and 92 per cent. of alcohol. In the case of uranous bromide or uranous chloride in water and methyl alcohol, it is found that the "water" and "methyl alcohol" bands are of about equal intensity when there are approximately 2 parts of water to 3 parts of methyl alcohol in the solution. In the case of the neodymium salts it would seem that the "water" bands are the more "persistent."

[1] Becquerel: Le Radium, Sept. (1907).
[2] Phys. Rev., **26**, 520 (1908). THIS JOURNAL, **41**, 163 (1909).

The less "persistence" of the "hydrate" of uranous chloride or uranous bromide may be due to the presence of the zinc salts formed during the reduction of the uranyl salts. It is found that the presence of free hydrochloric acid in a solution containing the "hydrate" and "methyl alcoholate" of uranous chloride causes the "water" bands to decrease in intensity with reference to the "methyl alcohol" bands. The action of any chloride would probably be the same. In the case of neutral salts of neodymium and uranium the "water" bands are usually more persistent than the "glycerol" bands, and these in turn are more persistent than the "alcohol" bands.

In the case of neodymium chloride in a mixture of 92 per cent. alcohol and 8 per cent. water it has been found[1] that Beer's law does not hold, the "water" and "alcohol" bands being of about equal intensity for a 0.5 normal solution, while for a 0.05 normal solution the "water" bands are much stronger than the "alcohol" bands. Whether the "water" bands in general show such a "persistence" is being investigated.

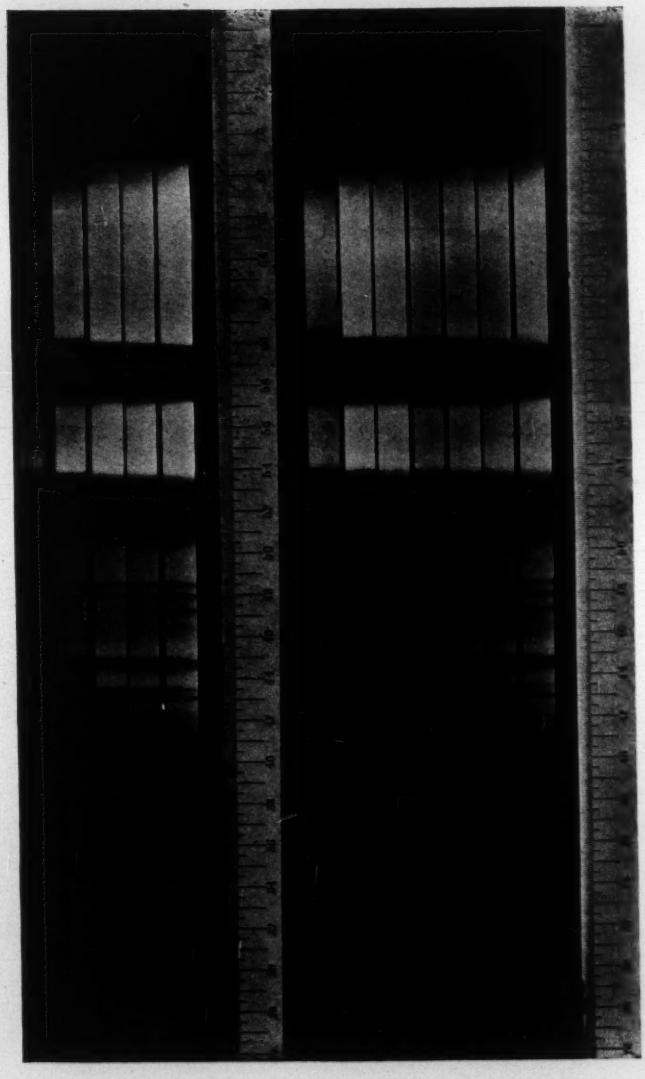
On the other hand, it has been found that the "alcoholates" are much more "persistent" than the "hydrates" at the higher temperatures. This is especially pronounced in the case of the "water" and "alcohol" bands of uranous chloride and uranous bromide. If the two sets of bands are of equal intensity at ordinary temperatures, at 80° the "water" bands have practically disappeared. This observation can easily be verified with a small pocket spectroscope.

Several very characteristic spectra have been obtained for neodymium salts dissolved in isomeric alcohols. The bands of neodymium chloride in isobutyl alcohol are of considerably greater wave length than the corresponding bands in butyl alcohol, whereas the "propyl alcohol" bands are displaced to the red with reference to the "isopropyl alcohol" bands. The "butyl" and "isobutyl" bands of neodymium nitrate are very much alike, while the "propyl" bands are displaced to the red as compared with the "isopropyl" bands, the displacement being in the same direction as for the chloride.

Neodymium Chloride in Water and Ethyl Alcohol.—A

[1] Physik. Z., **11**, 671 (1910); **12**, 269 (1911).

Plate XIX



A B

spectrograph was made representing the absorption of a 0.3 normal solution of neodymium chloride in water and methyl alcohol. The temperature range is from 30° to 80°. The original film shows that at the higher temperatures the water band λ 4271 almost disappears, while the alcohol band becomes stronger. The ε group shows the same thing in a general way, in that the total absorption, especially on the violet side of the band, is much less at the highest temperature than at the lowest temperature.

A spectrograph was taken showing the same effect for a more dilute solution. The finer water bands of the α, δ and ε groups are shown by the original film practically to disappear at the higher temperatures, while the alcohol bands become more intense.

Neodymium Bromide in Water and Methyl Alcohol.—A photograph was made representing the absorption of a neodymium bromide solution in methyl alcohol, 0.2 normal and 1.0 cm. in length. The variations in temperature were from 25° to 80°.

In the lower strip the alcohol band at about λ 4285 hardly appears at all, while the water band at λ 4271 is quite strong. At 80° the water band is still quite strong, and the alcohol band is possibly a third as strong as the water band.

Neodymium Chloride, Bromide and Nitrate in Water.—*B*, Plate XX, Strips 1, 2 and 3, shows the absorption of a 2.05 normal solution of neodymium chloride in water at 20°, 50° and 75°, respectively.

A, Plate XX, represents the absorption of a 1.66 normal aqueous solution of neodymium bromide at 20°, 40°, 60°, 80° and 93°, the highest temperature being that represented by the upper strip.

B, Plate XX, Strips 4, 5 and 6, represents the absorption spectrum of a 2.15 normal, aqueous solution of neodymium nitrate at 20°, 75° and 95°, respectively.

These spectrograms show the very great increase in the absorption of the short wave lengths as the temperature reaches about 90°. The spectrograms show the widening of the individual neodymium band. There is a slight shift

towards the red with rise in temperature, but this is very small. The absorption spectra of the three solutions are practically the same, that of the chloride and bromide being nearly identical, while that of the nitrate differs a little in some of the minute details of the individual bands.

Neodymium Chloride in Methyl Alcohol.—Plate XIX, *A*, represents the absorption of a 0.1 normal solution of neodymium chloride in methyl alcohol, 10 cm. in length. This spectrogram shows the methyl alcohol bands quite sharply. A weak band appears on the first strip at λ 4015, and at λ 4200. The band λ 4285 is quite strong and only about 10 Angström units wide. A weak and quite narrow band appears at λ 4270. The band λ 4270 is rather hazy; λ 4450 is about 50 Angström units in width and is very diffuse, its red side not being as diffuse as the violet side. The band λ 4620 is very weak; λ 4700, λ 4770 and λ 4820 all have about the same intensity and width, the first two being accompanied by very weak bands on their violet sides at λ 4680 and λ 4750. The band λ 5040 is very weak and broad; λ 5120 is about 20 Angström units wide and is very strong. The band λ 5175 is very similar to λ 5120, except that it is only about one-half as intense. The bands λ 5215, λ 5250 and λ 5290 are all very intense and are quite sharp, the middle band being about 20 Angström units in width, while the other two are only about 10 Angström units wide. There is a wide absorption band from λ 5710 to λ 5940, with the sharper edge on the violet side. The red band at λ 6850 appears to be quite strong and about 20 Angström units in width.

The other strips represent the same solution at different temperatures, these being 15°, 26°, 40°, 55° and 78°, starting with the lowest strip.

With rise in temperature the bands all become somewhat more intense and wider. The general absorption over the whole spectrum region increases, especially at the higher temperatures and begins to encroach quite rapidly on the violet and red regions. This violet absorption is probably a general absorption, but the encroaching on the red side is probably due to the increase in the intensity of the group of red bands.

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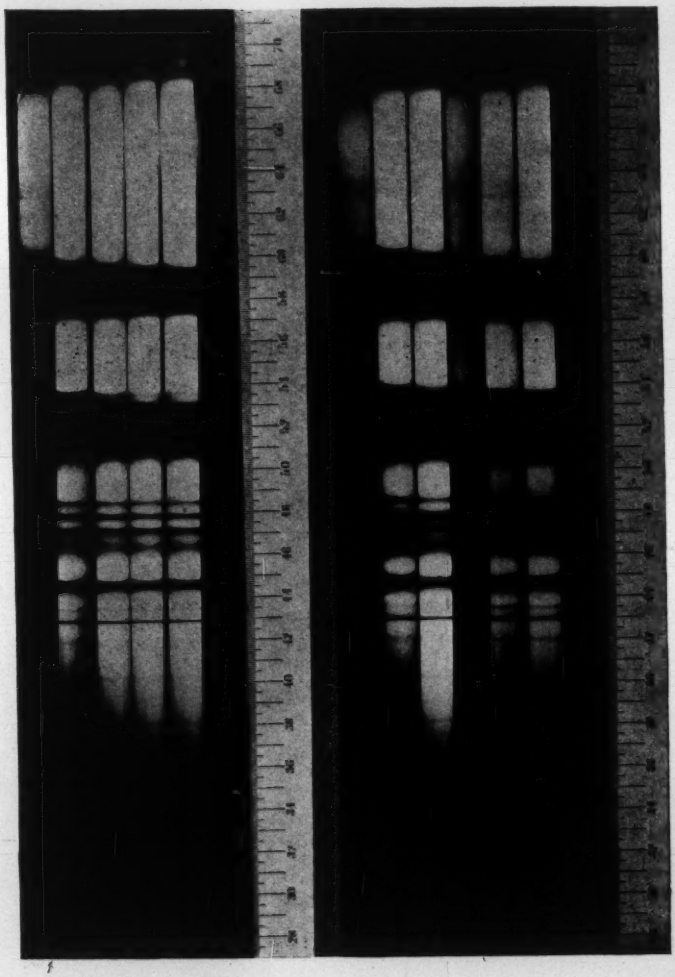
Plate XX



A B

In the upper strip transmission extends from about λ 4200 to λ 6100. A very weak band appears at λ 4200 and another one at λ 4305. The bands in the blue and green have changed but little. Absorption is pretty complete from λ 5100 to λ 5190, λ 5210 to λ 4350 and λ 5690 to λ 5990. Weak bands appear at λ 6230, λ 6280 and λ 6750. If any of the bands showed any shift it was too small to measure. The band at 15°, extending from λ 5710 to λ 5940, widens approximately 20 units on its violet side and 50 units on its red side. It is probably more or less general that wide absorption bands usually broaden unsymmetrically towards the red, especially when this side is the more diffuse.

A spectrogram representing the absorption of a methyl alcohol solution, 0.2 normal and 1.0 cm. in length, was made. The temperatures were 25°, 40°, 55° and 70°. The only important change due to temperature was at 70°, the intense absorption near the center of the ε group of bands having practically disappeared.

Neodymium Bromide in Methyl Alcohol.—B, Plate XIX, represents the absorption spectrum of a 0.1 normal solution of neodymium bromide in methyl alcohol. The length of cell was 10 cm. The temperatures were 25°, 35°, 44°, 60°, 82°, 100° and 120°, beginning with the lowest strip. At the highest temperature a slight precipitate was formed, but still some light was transmitted. The neodymium solutions all become much more deeply colored at the higher temperatures, as can easily be shown by heating such a solution in an ordinary test tube.

The absorption spectrum of neodymium bromide in methyl alcohol is quite different, as far as minute detail goes, from that of the chloride. In general, the bands of the chloride are from 5 to 15 Angström units farther towards the red than the bromide bands.

For the lowest strip, very weak and diffuse bands appear at about λ 4000, λ 4180, λ 4600, λ 4900, λ 5040, λ 5320, λ 6230, λ 6260, λ 6730 and λ 6790. The β group of the bromide is very different from that of the chloride. It consists of a very sharp, narrow (3 units) band at λ 4265, a very sharp and less

intense band at λ 4275, a hazy band at about λ 4280 which more or less overlaps λ 4275, and at higher temperatures λ 4275 can not be noticed at all. A very weak band appears at λ 4300, and a broader band, about 20 Angström units in width, at λ 4325.

The γ group of the chloride is also quite different from that of the bromide, which has four bands of almost equal intensity at $\lambda\lambda$ 4690, 4745, 4765 and 4815. Weak bands appear at λ 4670, λ 4700 and λ 4725. The δ group consists of a rather narrow band at λ 5090 and a very strong band at about λ 5115; a lot of narrow and intense bands at λ 5200, λ 5220, λ 5235; λ 5250 and λ 5275 practically merge into a single band. The ε group consists of a single wide band extending from λ 5700 to λ 5880.

As the temperature is raised the violet increases quite rapidly, and the δ and ε groups of bands become wider and stronger. The latter band widens very greatly towards the red. All the bands become very much more diffuse. This is particularly true of the β group, since at 120° only two very hazy, indistinct bands appear while at 25° some of the bands in this group were almost as fine as spark lines.

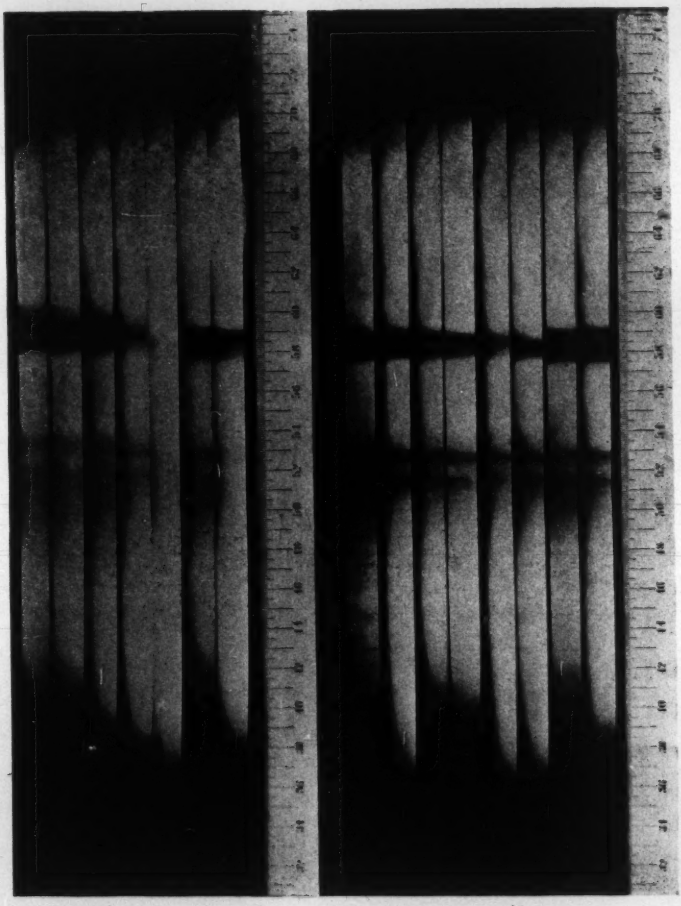
No measurable shift of the bands towards the red could be observed.

That the absorption spectra of the chloride and the bromide in methyl alcohol would be so different was quite unsuspected, since these two salts have almost identically the same absorption spectra in aqueous solution.

Neodymium Nitrate in Isobutyl Alcohol.—The absorption spectrum of a solution of neodymium nitrate in isobutyl alcohol was photographed at 20°, 45°, 75°, 95°, 110° and 120°. The concentration was 0.05 normal and the depth of cell 10 cm. The first strip of this spectrogram is described under the section on the mapping of spectra.

The general result of rise in temperature is to cause a large increase in the general absorption in the ultraviolet. This is especially strong at 120°, where the general absorption is complete to about λ 4100, and extends as a partial absorption to beyond λ 5000. The neodymium bands are considerably

Plate XXI



A B

widened by rise in temperature, and are shifted in many cases some 15 or 20 Angström units towards the red (120° compared with 20°).

Some of the more pronounced changes may be noted if the following wave lengths are compared with those described under the section on mapping of spectra. At 120° a weak band appears at λ 4260. It is about 10 Angström units wide. The other bands of the β group are at λ 4295, λ 4305, λ 4325 and λ 4360. The lines of the γ group are at λ 4725, λ 4775 and λ 4850. The δ group consists of the wide band at λ 5140 and the double band at λ 5250 and λ 5275. The ε group runs from λ 5720 to λ 5960 as a single band.

Neodymium Nitrate in Acetone.—A spectrogram was made of the absorption spectrum of a solution of neodymium nitrate in acetone, in the long cell, at 16°, 40°, 70°, 100° and 180°. The solution became opaque at about 110°, and afterwards quite transparent at about 160°.

The effect of the rise in temperature was to cause a slight shift of the neodymium bands to the red, but as these bands were so very broad and hazy, no measurements could be made. The strip taken at 180° shows a very great absorption in all regions except the yellow and red, and the absorption in the red is, indeed, almost complete. There is no indication of any neodymium bands at all, so that it seems that practically all the neodymium nitrate had been precipitated.

Erbium Chloride in Water.—*A*, Plate XXIII, represents, the spectrum of an aqueous solution of erbium chloride at 20°, 80°, 110° and 125°.

The effect of rise in temperature on the individual erbium bands is very small, their diffuseness being hardly increased with rise in temperature. The increase in the general absorption throughout the region of smaller wave lengths is enormous, resulting in the solution being practically opaque at the higher temperatures.

Strip 1 shows the following bands, the wave lengths being only approximate: a band from λ 3430 to λ 3520; a strong band at λ 3540 which is about 10 Angström units wide; weak bands at λ 3555, λ 3570 and λ 3595; the preceding band is the

beginning of a region of absorption that extends to λ 3660; a group of three bands that practically merge into a single band running from λ 3750 to λ 3790; weak bands at λ 3800 and λ 3840; diffuse bands at λ 3870 strong, λ 3900, λ 3950 weak, λ 4000 weak; λ 4045 sharp and narrow (10 units), λ 4070 sharp and narrow, λ 4100 very weak; $\lambda\lambda$ 4155, 4165, 4185, 4215—these bands are much alike, the first being the most intense; λ 4270 is wide and very weak, λ 4430 diffuse, λ 4450 very weak, λ 4480 weak, λ 4500 strong; λ 4530 is apparently covered by a diffuse band on its red side; λ 4685 weak, λ 4750 and λ 4800 wide and weak, λ 4855 narrow, λ 4880 intense, λ 4930 probably double, λ 5200, λ 5225, λ 5245 intense, λ 5290 weak, λ 5380, λ 5390 weak, λ 5435, λ 5455, λ 5520 weak, group at λ 5770 very weak, λ 6440, λ 6460, λ 6530, λ 6560 strong. The bands λ 6600 and λ 6710 are all very diffuse and have a very "washed-out" appearance.

Uranyl Chloride in Acetone.—A spectrogram was made of the absorption spectrum of a solution of uranyl chloride at 22°, 40°, 60°, 170°, 185° and 195°. At about 70° a precipitate was formed, but the solution became transparent again at 160°.

At 22° six of the uranyl bands appear, some being clearly double, as is characteristic of the acetone bands. At 40° only two bands appear, the general absorption throughout the violet and blue regions of the spectrum being so great. At 60° no uranyl bands appear at all, the short wave length absorption extending to about λ 5500. After the formation of the precipitate there is quite a strong transmission in the violet and about five uranyl bands appear. The uranyl bands are weaker and considerably narrower at the higher temperatures. Above 60° the bands appear to be single. From 170° to 195° the uranyl bands rapidly decrease in intensity, and at 195° they are so weak that it is not certain that they can be seen at all. At the same time the general absorption in the violet increases, but not to any great extent.

Uranyl Nitrate in Propyl Alcohol.—*B*, Plate XXIV, represents the absorption of a 0.005 normal solution of uranyl

Plate XXII

A B

nitrate in propyl alcohol, the depth of cell being 10 cm. The temperatures, starting at the lowest strip, are 20°, 40°, 65°, 85°, 105°, 115°, 130° and 145°. The sixth and seventh strips show a very weak transmission on the violet side of the blue-violet uranyl band. At 145° this has become a broad region of transmission. This spectrogram shows the enormous extension of the general absorption as the temperature rises.

The first strip shows the uranyl bands λ 4085, λ 4200, λ 4330 and λ 4470.

Uranyl Chloride and Nitrate in Isobutyl Alcohol.—A spectrogram representing the absorption of a 0.076 normal solution of uranyl chloride in isobutyl alcohol at 20°, 60°, 85° and 115° was made.

A photograph representing the absorption of uranyl nitrate of 0.033 normal concentration in isobutyl alcohol was made, the temperatures being 20°, 50°, 80°, 100° and 105°.

In the case of the chloride solution the uranyl bands are quite strong and fairly sharp. The two bands that show are at λ 4570 and λ 4730. In the case of the nitrate solution only a single band at about λ 4630 appears. This band is very diffuse and weak. For aqueous solutions, as will be remembered, the reverse is the case, the chloride bands being very weak and diffuse and the nitrate bands being quite strong and narrow.

Uranyl Chloride and Nitrate in Methyl Acetate.—A spectrogram representing a 0.005 normal solution of uranyl nitrate in methyl acetate at 20°, 50°, 75° and 100° was made. It shows that the uranyl bands are quite strong and clear. As the temperature rises the general violet absorption increases, and the uranyl bands are slightly shifted towards the red. The approximate wave lengths of some of the bands are $\lambda\lambda$ 3900, 4020, 4130, 4250, 4380, 4520, 4670 and about 4820, this last band being very weak.

A photograph showing uranyl and calcium chlorides in methyl acetate, and uranyl and calcium chlorides in methyl alcohol, was taken.

The temperatures were 20°, 45°, 85°, 20°, 50° and 95°. The methyl ester at 20° showed very strong bands at $\lambda\lambda$ 4600, 4760 and 4930.

It was thought that if a large amount of a salt like calcium chloride were added to solutions of uranyl chloride in different solvents, the absorption spectra of the resultant solutions would be more nearly alike. This spectrogram shows that this is not the case, since in the lower strips the uranyl bands are very strong and quite sharp, whereas in the case of the methyl alcohol solution the bands are very wide and very weak. Their wave lengths are also considerably greater than those of the bands in the ester solution. These spectrograms show that although double salt aggregates may be formed, the solvent part of the aggregate still plays a very important role in influencing the wave lengths of the absorption bands.

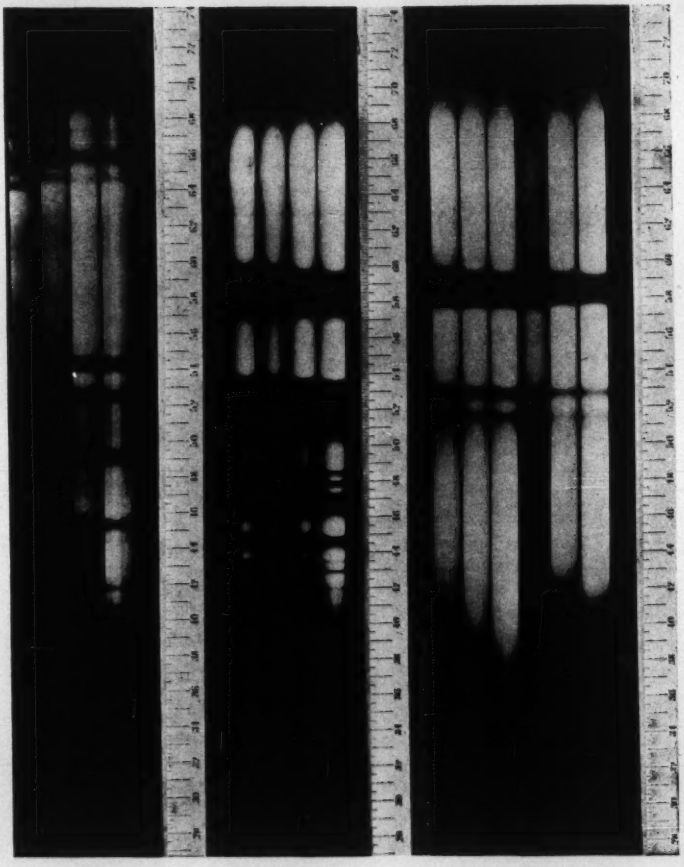
The effect of the addition of calcium chloride to the ester solution was not tested by regular steps, but for the pure uranyl chloride solution the α band appears as a double band with the components at about λ 4930 and λ 4965. These bands practically merge into one another, and it is rather difficult to see that the band is really double. Apparently the effect of the addition of calcium chloride is to cause the component λ 4965 to disappear, and, at the same time, the other component widens. The methyl ester solutions offer a promising field for studying the spectrophotography of chemical reactions and also the effect of dilution.

A, Plate XXIV, represents the absorption of 0.005 normal solution of uranyl chloride in methyl acetate, the depth of cell being 10 cm. The temperatures, starting with the lowest strip, are 20°, 45°, 70°, 90°, 110°, 135° and 140°.

At 20° the following uranyl bands appear: λ 3930 fine and weak; λ 4050 quite narrow; λ 4170, λ 4300, λ 4450, λ 4630 and λ 4800 probably the *b* band. At 140° only the *b*, *c* and *d* bands appear at $\lambda\lambda$ 4480, 4650 and 4820. At the highest temperature the transparency of the solution in the violet has apparently increased. The character of the uranyl bands is but slightly affected by the above temperature changes.

Uranous Chloride in Water and Methyl Alcohol.—Strip 5, *A*, Plate XXV, represents the absorption of uranous chloride in a mixture of water and methyl alcohol in such proportions that the water and alcohol bands were of about equal in-

Plate XXIII



A B C

tensity at 10°. Strip 6 represents the same solution at about 70°.

These strips show that at the higher temperature the uranous water bands have almost disappeared. The uranyl bands have also become very much weaker, and the uranous alcohol bands slightly weaker. No appreciable shifting of the bands is to be noticed.

Uranous Chloride in Acetone.—A spectrogram of the absorption spectrum of uranous chloride in acetone was taken at 20°, 40°, 65°, 80°, 95° and 105°.

At about 60° a precipitate was formed, and above this temperature the red absorption band hardly appears at all. The uranous bands in the green and yellow seem to be considerably stronger after the formation of the precipitate.

The Existence of Aggregates and their Properties, and the Effect of Rise in Temperature on the Aggregates

The presence of free acid[1] or of other salts has been found to modify very considerably, in many cases, the uranyl, uranous and neodymium bands of a given salt in solution. Up to the present, work of this kind has been practically restricted to aqueous solutions, although similar changes take place in other solvents. One of the most pronounced cases is that of the uranyl nitrate and the uranyl chloride bands. Most of the nitrate bands have shorter wave lengths than the chloride bands. As increasing amounts of hydrochloric acid are added to an aqueous solution of uranyl nitrate, the nitrate bands are found to shift gradually into the position of the chloride bands. Furthermore, the addition of nitric acid to an aqueous solution of uranyl nitrate causes most of the uranyl bands to shift towards the violet, whereas the addition of hydrochloric acid to an aqueous solution of uranyl chloride causes most of the bands to shift toward the red. These changes are quite different from those that take place when the solvent is changed; and if it is supposed that a characteristic absorption spectrum corresponds to a more or less stable compound, then these changes indicate a series of compounds which will be referred to as aggregates. We

[1] Physik. Z., **11**, 668 (1910); **12**, 269 (1911).

would have, then, nitric acid aggregates of uranyl nitrate, or hydrochloric acid aggregates of neodymium chloride.

Whether there is an actual change in the frequency of vibration for a series of uranyl or uranous aggregates, or whether there is simply a relative change in the intensity of a number of finer bands which blend into the rather broad and diffuse bands that are photographed, can not be decided at present. In the case of neodymium salts[1] the various spectrophotographs indicate the latter effect. It is unlikely that the case can be settled very easily for uranyl and uranous salts, since the greatest shifts take place in the absorption of aqueous solutions and these can not be studied at very low temperatures. Subsequently, it will be assumed that a spectrogram of a chemical reaction, showing a gradual shifting of bands, indicates the presence of a series of closely related aggregates existing in the solution.

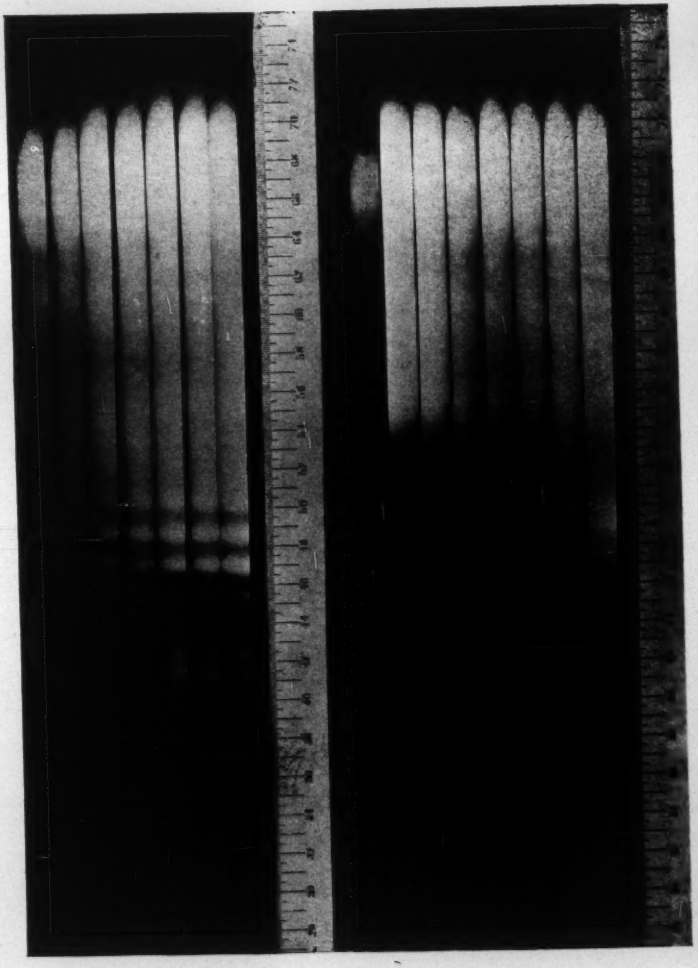
The mixture of varying proportions of two neutral salts in a solution may result in a gradual change from the bands of one salt into the bands of the other salt (mixtures of uranyl nitrate and uranyl chloride in water). On the other hand, there are cases in which each salt seems to have its own definite spectrum. In this case there will be no shifting of the bands but only a change in intensity, and we may assume that, in this case, there are no double salts formed. In the former case, however, it seems probable that there are aggregates formed which contain one or more molecules of each salt.

The addition of salts[2] containing the same cation as the corresponding uranyl or uranous salt has an effect similar to that of the addition of free acid, and may be considered as indicating the presence of aggregates. In the case of uranyl chloride the effect seems to be due largely to the chlorine present.

Acid aggregates of uranous salts are found to be much more stable than the neutral aggregates. Uranous nitrate, for example, is very unstable, but uranous chloride dissolved in concentrated nitric acid will stand for hours before it is oxidized

[1] Physik. Z., **11**, 671 (1910); **12**, 269 (1911).
[2] Publication No. 130, Carnegie Institution of Washington, p. 91.

Plate XXIV



A B

to the uranyl condition. Most of the neutral uranous salts are precipitated when heated to 80° or 90°; but if some free acid, or, in the case of uranous chloride, other chlorides are present, the uranous salts are stable at these higher temperatures.

It might be expected that if the effect of rise in temperature is to break up aggregates, then in the case of concentrated acid solutions of the uranyl salts the shift towards the red should be very great for a concentrated nitric acid solution of uranyl nitrate; while in the case of a hydrochloric acid solution of uranyl chloride, or of a sulphuric acid solution of uranyl sulphate, the shift should be in the opposite direction. On the other hand, if the shift caused by change in temperature is due to some other cause and the aggregates are not broken up, no effect of this kind would be expected.

In a solution of uranous sulphate in sulphuric acid the uranyl bands are slightly shifted to the red as the temperature is raised from 10° to 90°, while the uranous bands are slightly shifted to the violet. The shift of the neutral uranyl sulphate bands to the red is greater than that of the acid sulphate bands. The shift of the uranyl nitrate bands in nitric acid is about 15 Angström units. All bands are shifted about the same amount

Neodymium Salts in Acid Solutions.—Plate XXII, *A*. This spectrogram shows the effect of hydrochloric acid, sodium chlorate and temperature on the neodymium chloride bands. Strip 1 is the absorption of neodymium chloride in water at about 10°, Strip 2 the same at about 90°. Strip 3 represents the absorption of the same amount of neodymium chloride in concentrated hydrochloric acid at 10°, Strip 4 at 90°. Strip 5 represents the absorption at 10° of neodymium chloride in methyl alcohol, and Strip 6 of the same containing sodium chlorate.

Plate XXII, *B*. This spectrogram shows the absorption of a 0.02 normal solution of neodymium acetate at 10° in Strip 1 and at about 90° in Strip 2. Strip 3 represents the absorption of a small amount of neodymium chloride added to acetic acid so as to fill the quartz cell at 10°, and Strip 4

the same at 90°. Strip 5 represents the absorption of neodymium acetate in acetic acid at 10°, and Strip 6 the same at about 90°. Strip 7 represents the absorption of a solution in methyl acetate and acetic acid at 10°, and Strip 8 the same at 90°.

The first two strips in *A* show that the effect of rise in temperature on an aqueous solution of the chloride is to cause a very slight shift of the bands towards the red, and to give them a much more diffuse and washed-out appearance. The hydrochloric acid solution of neodymium chloride shown in Strips 3 and 4 is but very slightly changed by rise in temperature, and there is no indication that the spectrum becomes more closely like that of the neutral aqueous solution. The shift to the red is very small. It can easily be noticed for the bands of the ε group. At 10° the long wave length bands of the γ group are very much like the two bands of the neutral aqueous solution. At 90° these bands have both become very diffuse, blending into a single band, and the whole center of the band is greatly shifted towards the red. This is the greatest temperature change in the whole spectrum. The presence of sodium perchlorate in a methyl alcohol solution of neodymium chloride causes the neodymium bands to be shifted very slightly towards the violet.

A neutral acetate solution in water, as shown in Strips 1 and 2 of *B*, is affected like the neutral chloride solution in that at the higher temperature the bands have a much more diffuse, washed-out appearance. This is especially true of the α group, which appears very weak at 90°. Very little shifting of the bands towards the red takes place. Strips 4 and 5 show about the same effect, and the same very great decrease in the intensity of the α group at the higher temperature. In the next two strips the α group remains of about the same intensity at the two temperatures. There is less increase in the diffuseness of the acetate bands in acetic acid than in the case of a neutral acetate solution.

Plate XXI, *A*. This spectrogram represents the absorption of neodymium chloride in acetone at 10° (Strip 1) and at 90° (Strip 2); neodymium chloride in ether at 10° (Strip 3; a

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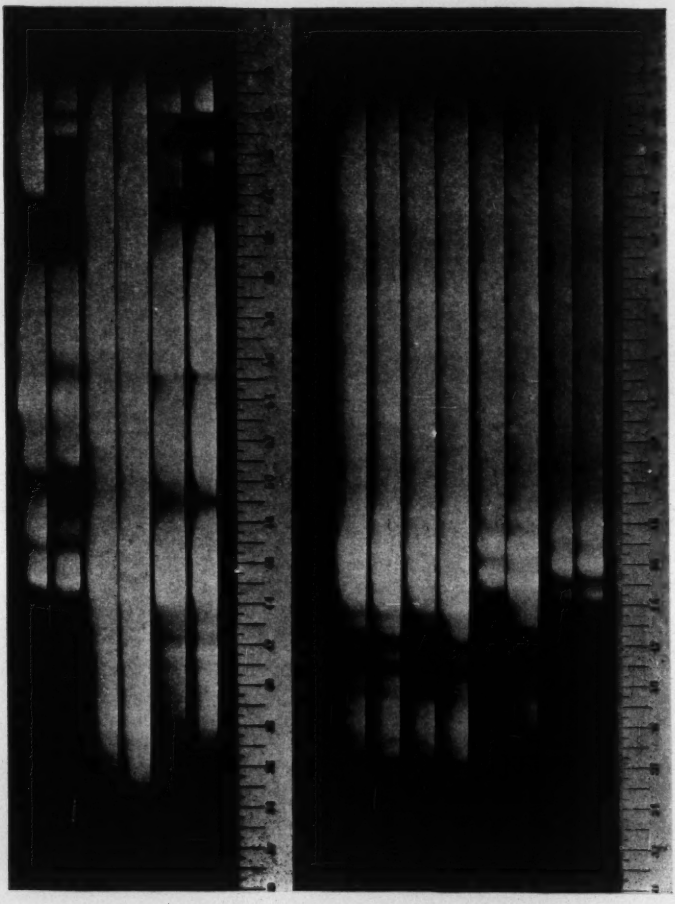
Plate XXV



A B

precipitate is formed at higher temperatures); 0.02 normal neodymium chloride in ethyl alcohol at 10° (Strip 4) and about 70° (Strip 5); neodymium chloride in ethyl alcohol to which hydrochloric acid gas has been added at 10° (Strip 6) and at about 70° (Strip 7).

Plate XXI, *B*. This spectrogram represents the absorption of neodymium nitrate in nitric acid at 10° (Strip 1) and at about 50° (Strip 2; if heated to much higher temperatures nitrous oxide is formed); of neodymium chloride in methyl alcohol and 8 per cent. of water at 10° (Strip 3) and at about 70° (Strip 4); neodymium nitrate in acetone and 8 per cent. water at 10° (Strip 5) and at about 60° (Strip 6); neodymium chloride in 60 per cent. ethyl alcohol and 40 per cent. water at 10° (Strip 7); and neodymium chloride in 40 per cent. water and 60 per cent. glycerol at 10° (Strip 8).

The acetone solution of neodymium chloride shows very little if any change with rise in temperature. The ethyl alcohol solution shows a small increase in the diffuseness and a very great shift of the intensity of the band groups with rise in temperature. When hydrochloric acid is present there is very little change of this kind. The new and very strong bands appear at about λ 3590 and λ 3750, the latter being about 50 Angström units wide.

The nitric acid solution of neodymium nitrate shows very little change in the absorption spectra with rise in temperature. The bands become somewhat more diffuse and decrease in intensity. The red bands do not show in the strips. Strips 3 and 4 show the very considerable increase of the alcohol bands over the water bands. The fine α, β and δ water bands have practically disappeared at the higher temperature.

Uranous Sulphate in Sulphuric Acid.—Plate XXV, *A*. The absorption of uranous sulphate in sulphuric acid at 10° is represented in Strip 1, and at about 90° in Strip 2. The absorption of the neutral uranous sulphate in water at 10° is shown in Strip 3, and at about 80° in Strip 4. The absorption of uranous chloride in water and in methyl alcohol, at 10°, is shown in Strip 5, and at about 70° in Strip 6. The uranyl bands of the sulphuric acid solution are shifted towards

the red with rise in temperature, whereas the uranous bands seem to be shifted slightly towards the violet.

Uranyl Nitrate in Nitric Acid, Uranyl Chloride in Hydrochloric Acid and Uranyl Sulphate in Sulphuric Acid.—Plate XXV, *B*. The absorption of uranyl nitrate in nitric acid at 10° is represented in Strip 1, and at about 70° in Strip 2; of uranyl chloride in hydrochloric acid at 10° in Strip 3, and at about 80° in Strip 4; of uranyl sulphate in water at 10° in Strip 5, and at about 90° in Strip 6; of uranyl sulphate in sulphuric acid at 10° in Strip 7, and at about 90° in Strip 8.

Each one of the uranyl nitrate bands seems to be shifted, due to the rise in temperature, about 10 Angström units towards the red, the uranyl chloride bands in hydrochloric acid being shifted about 15 Angström units.

In the case of uranyl sulphate, only the uranyl bands in the region of the blue-violet band were greatly shifted towards the red with rise in temperature. The shift seemed to be considerably greater for the neutral than for the acid solution.

According to the aggregate theory we might expect that if the uranyl nitric acid aggregates break down at the higher temperatures, the uranyl bands would be very greatly shifted towards the red on account of less nitric acid molecules affecting the uranyl vibrations. But this does not seem to be the case to any very great extent, since here the shift to the red is not any greater than for the other uranyl bands, and seems to be about the same for each one of the bands. It may be considered that the hydrate is more simple, however, and that this allows more of the nitric acid molecules to come within the range of the absorbing centers, and this might in a way counteract the effect of any decomposition of aggregates. Whether the effect of an increase in the number of molecular collisions brings a greater number of nitric acid molecules within the effective range of the absorbing centers, and has an effect on the frequency, can not be decided from the spectrograms.

The very considerable shift of each one of the uranyl chloride bands of the hydrochloric acid solution towards the red with

rise in temperature probably indicates that there is very little decomposition of the uranyl chloride acid aggregates.

Since apparently onyl the *e*, *f*, *g* and *h* uranyl sulphate bands are greatly shifted towards the red, we might assume that there is a slight decomposition of the uranyl sulphate aggregates, and this counteracts what we might call the normal temperature shift.

In the above strips temperature has very little effect on the uranyl bands, except a shifting of their wave lengths towards the red.

GENERAL DISCUSSION OF THE MOST IMPORTANT RESULTS

Mapping of Spectra

The first problem to be solved in a study of absorption spectra is the recording of the spectra themselves. The method employed in this series of investigations is that of photographing the absorption spectrum of a solution placed in a beam of light having a continuous spectrum. Such a photograph may be called a spectrogram or a map of the given absorption spectrum.

The study of the spectrograms of colored solutions shows that this color is due to a selective absorption of the solution in some part of the spectrum; and the extent of this selective absorption may be over regions of the spectrum hundreds of Angström units in width, or over regions only a fraction of an Angström unit wide—a width that is not much greater than that of a spark or arc line. In fact, bands of almost all widths and degrees of diffuseness are found in addition to the absorption, which is one-sided. If the region of one-sided absorption lies in the red, it is probable that it has another edge in the infrared. Practically all solutions show an encroaching general absorption in the ultraviolet as the amount of the solution in the path of the light is increased or as the temperature is raised.

The plates and the description of these plates in Publications Nos. 60, 110, 130 and 160 of the Carnegie Institution of Washington give a pretty thorough representation of the de-

tails of the absorption spectra of most of the typical solutions of the colored inorganic salts.

It can be said, in general, that the absorption spectra of the various salts of the same element are very much alike; indeed, so much alike that it is only when considerable dispersion is used that any differences can be noted. It can also be said that the absorption spectra of the same salt in various solvents are very similar. For these reasons we are justified in assuming that the color of solutions of colored salts dissolved in colorless solvents is due primarily to the metal or metallic radical of the colored salt. The various spectra that are characteristic of a given kind of salts, say the uranous salts, will, therefore, be called the uranous spectra.

In the mapping of the absorption spectra of solutions of increasing concentration or of increasing depth, it is always found that the absorption bands widen and become more intense as the amount of salt in the path of the beam of light is increased. It can also be stated, as an approximately general law, that the more diffuse a band is the greater will be the widening under these conditions. Examples of this kind are shown by the uranous bands, which may widen from fifty or a hundred Angström units to a width of thousands of Angström units. The widening of single, very sharp bands with increasing amounts of the salt in the path of the light is invariably small. As an example we can take the λ 4271 neodymium chloride water band.

When characteristic absorption spectra of salts of the rare earths, of cobalt, chromium, etc., are studied with the use of a high-dispersion spectroscope, it is found that the finer absorption bands are different for the same salt in different solvents, and for different salts in the same solvent. This difference may be a difference in the number of the bands present, a difference in the intensity and width of the bands or a difference in wave length.

It can be said, in general, that the absolute differences of intensity, diffuseness and wave length, under these conditions, are greater for the larger and the more intense bands. Unfortunately, the very large bands are usually so situated in the

spectrum that only small changes in the amount of salt can be made before the band becomes one-sided, on account of the comparatively small region of the spectrum that can be investigated by photographic methods. But it can be said that the uranous bands show greater changes with change of salt or solvent than the uranyl bands, that the uranyl bands show greater changes than the neodymium bands and that these, in turn, seem to show much greater changes than the dysprosium and samarium bands, and these, finally, probably greater changes than the erbium bands.

When we consider the minute structure of the bands and groups of bands under high dispersion, we find very great differences, especially in the case of neodymium. The different salts of neodymium in the same solvent, especially in some of the organic solvents, give entirely different absorption spectra. The same is true of the same salt in different solvents. Isomeric solvents very often show characteristic spectra. The absorption bands of neodymium have been divided into groups α, β, γ, δ, ϵ, etc. When there is a large amount of salt in the path of the beam of light, each group usually forms a single broad band. It is found that the relative intensities and characteristics of these groups are very much the same for different salts in different solvents. The minute structure of the bands in the same group is usually more widely different than the absorption spectra of dysprosium and samarium, so that it is quite probable that if the region of spectrum that we could study were wide enough to include one of these groups, and sufficient dispersion were used we would consider that we were dealing with different elements whenever the salt and the solvent were changed.

The spectrograms and the descriptions in detail give a large number of examples illustrating the above. Very much more work of this kind remains to be done with solutions like those of neodymium at low temperatures, very high dispersion being used.

From the above description of absorption spectra it follows at once that any law, such as the supposed law of Kundt, connecting the wave length of the absorption band with the

value of the dielectric constant of the solvent is impossible.

Beer's law is found to hold approximately for nearly all solutions of a single neutral salt in a single solvent. Exceptions are found when very concentrated solutions are used, and with only one known exception (solutions of uranyl acetate give a very large negative deviation) the deviation is such that when the concentration is increased the absorption is greater than would be given by Beer's law. The fact that Beer's law holds indicates that, as far as our knowledge of absorption spectra is concerned, there is no difference between ions and molecules. It therefore can not be said, in general, that for solutions showing characteristic bands there is any part of the spectrum due to ions or any part due to molecules. Yet the work of Jones and Anderson[1] showed that certain bands are probably due to certain constituents of the molecules, such as the atom, the hydrate, etc.

A Theory of Absorption Spectra

It is natural to try to correlate as many spectra as possible, and this has been done in a number of cases. For organic compounds, benzene for example, it is found that the ultraviolet absorption spectra in the gaseous, in the liquid and in the dissolved states are very similar. It is therefore natural to endeavor to test colored salts in the same way. Unfortunately, no metallic salts having a characteristic absorption spectrum can be obtained in the gaseous state. As pure salts, in solutions and in transparent solids, however, the absorption spectra of salts of the same element are very much alike as far as the grosser structure is concerned. None of the vapors of the metals of these salts can be obtained unaccompanied by the effects of high temperature and intense ionization. It is for this reason that the branch of spectroscopy dealing with the absorption spectra of inorganic solutions is quite completely separated from the other branches of spectroscopy.

However, a study of other branches of spectroscopy will be of considerable importance in helping to give us a working

[1] THIS JOURNAL, **41**, 163 (1909). Publication No. 110, Carnegie Institution of Washington.

hypothesis concerning the material centers that are absorbing or emitting light.

An emission or absorption center of light and heat will be defined as the smallest particle existing by itself that is capable of emitting or absorbing a given characteristic spectrum. Until proved to be an ion, an atom, a molecule or an aggregate of these, we can not assume that the division of matter into emission and absorption centers is at all identical with the division of matter into ions, atoms and molecules. In a study of these light centers one of the most difficult problems that confronts us is the complete separation of individual light centers, and it is owing to this fact that our knowledge of these light centers is so meager. An example of this kind might be taken in the more or less independent series of lines as classified by Kayser and Runge, Ritz and others. It has never been proved that there are separate emitters and absorbers for each one of these series of lines, neither can it be said that these centers correspond to atomic, ionic or molecular units. It may be that each series of lines is due to a system, and that several systems are joined together to form an absorption or emission center, but these systems can not exist as separate units and still act as light centers. The same condition probably applies to the systems that give rise to the simple series of fluorescent bands discovered by Wood, so that there would not be a different absorption center for each one of these series of bands, but there is one type of absorbing centers that contains several absorbing systems that can be separately excited, and as soon as the absorbing center is broken into parts it loses its characteristic absorption spectrum.

It seems quite probable that many of the systems in the light centers contain electrons, and it is probable that it is these electrons that give the Zeeman effect. The electrons that are indicated by the Zeeman effect of arc and spark lines are but slightly affected by external forces, so that it has been very generally assumed that these form parts of systems that make up the fundamental structure of the ultimate units of matter. Indeed, a characteristic spectrum has been used

as defining an atom; and, in general, it has been found that a characteristic arc and spark spectrum accompanies matter which, according to other physical and chemical methods, is believed to be composed of exactly the same atomic units. It is for this reason that the assumption is generally made that the absorption and emission centers of these arc and spark spectra are either the same as the atoms of the element, or contain one or more atoms of the element.

In making an assumption of this kind two of the greatest difficulties encountered are the complexity of the spectra that are found to be characteristic of an element and the fact that the light centers seem to exist, or at least are active, only under certain conditions. The first problem is answered by supposing that if the light center corresponds to the atomic unit of matter, then there are subatomic systems that correspond to the various spectra. Very little evidence of such subatomic systems is at hand, yet the present theory of radioactivity gives very strong support to this view and indicates that, whenever these subatomic systems are separated, entirely new atomic units are formed, and that one atomic unit may consist of several smaller atomic units. The second problem is illustrated by many examples, a good one being that of sodium. The sodium atoms exist under conditions that make them parts of entirely different light centers. The sodium atom may form part of the absorbing or emitting centers of the arc or spark spectra, the emitting centers of a certain vacuum discharge spectrum, the absorbing centers of the fine-banded absorption spectrum, the emission centers of the fluorescent spectrum, etc. The sodium atoms may also exist in various molecules and be perfectly transparent in the visible part of the spectrum. Suggestions have been made only as to what the constitution of the light centers of these spectra may be, and these suggestions have usually been based on the assumption that these light centers consisted of atomic or molecular complexes.

Most light centers seem to be formed only during very exceptional physical and chemical conditions, so that they have been often considered as being very unstable, and that

an atom or molecule forms a part of a light center only during a small part of the time. This view is strengthened by the theory of absorption and dispersion, according to which it often happens that the number of electrons taking part in the absorption or emission of light is much less than the total number of atoms or molecules present in the matter that is either emitting or absorbing the light. Exactly what conditions are necessary for producing light centers? Some evidence has been accumulated which indicates that these conditions may be furnished by the dissociation or recombination of parts that form complex molecules. These are apparently the conditions under which the light centers of the fine iodine, bromine, sulphur, chlorine, etc., bands exist.

The length of duration of the fluorescent and phosphorescent bands of solids and liquids furnishes a method of analysis of spectra in that the duration of different bands after the excitation has ceased is very different. No relations have, however, been found between fluorescence and phosphorescence and the conductivity, so that the current theories are based on the assumption that the light centers are very complex molecular aggregates (Lenard and Klatt) and that the dissociation or recombination effects take place within these aggregates.

The absorption spectra of organic compounds support the view that the absorbing centers in these cases are generally complex. These centers are called chromophores, and as a rule they form only a part of the molecular structure. Unfortunately the absorption spectra of chromophores are not characteristic, so that the whole study is more or less a colorimetric one. The peculiar conditions under which the absorption centers are active has been assumed to be the same as those accompanying phenomena that are explained by the theory of dynamic isomerism, and consist in a supposed change of the interlinking of radicals in the organic compounds. If valency is of an electromagnetic nature, a condition of dynamic isomerism would also be a condition of intramolecular ionization.

The absorbing centers of inorganic salt solutions are prob-

ably somewhat similar in nature to the absorption centers found in the case of solutions of organic compounds, the phosphorescent compounds of the rare earths studied by Goldstein, Kowalski and others. Every characteristic absorption spectrum will be considered as evidence for the existence of a compound, and these compounds will be called *aggregates* and may be assumed to consist of one or more molecules or ions of the dissolved salt and one or more molecules of the solvent. That the number of these aggregates seems to be quite large is no evidence against the theory of aggregates, since there is no reason why an element like uranium should not form a very large number of compounds.

As a typical example of an aggregate, we will take a mixture of two kinds of dissolved compounds in a mixture of two solvents. Assuming that the UO_2 group can act as an ion and that it carries a double charge, a general formula for aggregates would be the following:

$$x\{UO_2SO_4\}y\{H_2SO_4\}u\{\overset{++}{UO_2}\}v\{\overset{+}{H}\}w\{\overset{--}{SO_4}\}a\{H_2O\}$$
$$x'\{UO_2SO_4\}y'\{H_2SO_4\}u'\{\overset{++}{UO_2}\}v'\{\overset{+}{H}\}w'\{\overset{--}{SO_4}\}b\{CH_3OH\}$$

We may assume that at ordinary concentrations u, v, w, u', v' and w' have small values. Whenever a definite and characteristic absorption spectrum is obtained it will be assumed that the absorption centers are aggregates of a definite composition, and that all the coefficients in the above equation have a definite value.

From the fact that absorption centers are found in solids such as the various glasses and crystals, it must be assumed that the existence of active absorption centers need not be connected with any conducting particles. On the other hand, the work of Becquerel and others seems to indicate that the number of absorbing centers is much smaller than the number of atoms present. If the aggregates are very complex, then the number of absorbing centers would be much less than the number of molecules of the colored salt. This would probably require very large values for x and x', and, therefore, makes this view improbable. On the other hand,

it is not necessary to assume that the aggregate is an active light center all the time, but that the aggregate is only active while it is in a peculiar condition. This peculiar condition may be assumed to be a kind of internal ionization, somewhat similar to that which is assumed in the theory of dynamic isomerism, or in the theory of Lenard and Klatt. For instance, electrons may pass back and forth within the UO_2 group, or between the UO_2 and surrounding groups. The system whose vibrations give rise to the uranyl group is probably located in the uranyl radical, and possibly in the uranium atom itself. When an electron is ejected, or when it recombines with the UO_2 group, it may be considered that the system absorbs light and is then an active center. When the absorption takes place, the frequency of the absorption bands and their width and intensity will depend on the structure of the aggregate—i. e., on the values of x, y, u, v, w and a.

In a spectroscopic study of the aggregates found in salt solutions, it may be said that the absorption spectrum indicates only a condition of a small part of the salt. In other words the values of x, y, u, v, w, a, etc., may be functions of the time. In order to solve this problem it will be necessary to study the nature of the aggregates by other methods; and if widely different methods give the same values for x, y, u..., etc., it may then be assumed that the value of these variables is not a function of the time.

In the present treatment it will be assumed that these spectroscopic aggregates represent the statistical average condition of the dissolved salt molecules, and although these aggregates may be active absorbing centers for a small part of the time it will be assumed that the difference between an absorbing and a nonabsorbing aggregate, if such there be, is not due to any change in the values of x, y, u, v, w, a, etc. The intensity of a given absorption spectrum will be assumed to be a measure of the amount of the aggregate present in the solution that corresponds to the given absorption spectrum. In every known example it has been found that the changes in the values of x, y, z, a, etc., produce changes that indicate

that each characteristic spectrum is due to a system whose parts form one organic whole.

The Uranyl and Uranous Bands

The uranyl spectrum consists of some twelve bands starting from λ 5000 and runs into the ultraviolet. Starting with the long wave-length band they have been designated by the letters *a*, *b*, *c*, etc. These bands form a series, the distance between the bands decreasing with the wave length. The uranous bands do not form any series, and resemble the uranyl bands only in their general appearance. The uranium bands are quite wide and diffuse as compared with the erbium and neodymium bands. A considerable amount of confusion has been caused in the past by the fact that most of the uranous salts contain uranyl salts mixed with them, and, therefore, their absorption spectra include the uranyl bands. The complete independence of the two sets of bands is very clearly shown on spectrograms of the absorption spectra of a uranous salt as it is gradually oxidized to the uranyl salt by the addition of hydrogen peroxide.

(1) A problem of considerable interest, and one for which an answer[1] has been partly obtained, is the complete correlation of the *a*, *b*, *c*, etc., bands when one uranyl salt is transformed into another salt, or when the solvent is changed. Thus, for instance, the *a* band could be traced from the nitrate to the sulphate, acetate, etc., and also for these salts in various solvents. It may be that the neodymium, erbium and samarium bands can be studied in the same manner, especially at low temperatures. The results of such a study should extend very greatly our knowledge of chemical reactions.

(2) If uranyl chloride and calcium nitrate are dissolved in water, uranyl chloride and uranyl nitrate should both be present in the solution. In terms of the theory of aggregates, then, it would be expected that the addition of calcium nitrate to an aqueous solution of uranyl chloride would cause the uranyl chloride bands to shift towards the violet. On the other hand, the addition of aluminium or calcium chloride

[1] Publication 130, Carnegie Institution of Washington.

to an aqueous solution of uranyl nitrate should cause the uranyl nitrate bands to shift towards the red. The experimental results verify these conclusions.

Preliminary spectrograms showed that the addition of calcium nitrate to an aqueous solution of uranyl nitrate caused the uranyl nitrate bands to shift slightly towards the violet, the amount of the shift, however, being very small. This seems to show that calcium itself has very little, if any, effect upon the absorption, and this is in agreement with the results of Becquerel and others.

(3) When an acid is added to a neutral uranyl salt in sufficient quantity, this salt is changed to a salt of the acid added. Up to the present no quantitative study of the strengths of acids has been made by the spectroscopic method, but by means of radiomicrometric measurements this method should give a reasonably accurate means of measuring the relative strengths of various acids, especially in aqueous solutions.

(4) The *modus operandi* by which uranyl are transformed into uranous salts, and *vice versa*, is not known. This subject has, however, been discussed in the section dealing with the spectrophotography of chemical reactions. It seems probable that there is not the usual dynamic equilibrium between the uranyl and uranous salts.

Aggregates and their Properties

(1) The presence of free acid or of foreign salts[1] has been found to change the frequency of many of the uranyl, uranous and neodymium bands. At present our knowledge of these effects is practically restricted to aqueous solutions, although similar effects are known to occur in other solvents. An example of the above effect is that of the uranyl chloride and nitrate bands. The wave lengths of the uranyl nitrate bands are considerably smaller than those of uranyl chloride. This has been shown to be due to the presence of NO_3 and H_2O groups in the absorbing centers of the nitrate in solution. On the addition of hydrochloric acid to an aqueous solution of uranyl nitrate, the uranyl nitrate bands shift gradually to the

[1] Physik. Z., **11**, 668 (1910); **12**, 269 (1911).

positions of the uranyl chloride bands. The addition of more hydrochloric acid causes most of the uranyl bands to continue to shift towards the red. On the other hand, the addition of nitric acid to an aqueous solution of uranyl nitrate causes the uranyl bands to shift towards the violet. We thus obtain a gradual shifting of the uranyl bands of a nitric acid solution of uranyl nitrate into the position of the uranyl bands of uranyl chloride dissolved in concentrated hydrochloric acid. The magnitude of this shift is shown by the following wave lengths:

	Uranyl bands						
	a	*b*	*c*	*d*	*f*	*g*	*h*
Nitrate in nitric acid	4790	4670	4510	4370	4125	4000	3900
Chloride in hydrochloric acid	4950	4800	4635	4450	4280	4050	4015

These changes are quite different as compared with those that take place when the solvent is changed, and if it is assumed that every characteristic absorption spectrum corresponds to a more or less stable system, then the above changes indicate the existence of a series of systems or compounds. These compounds will be called aggregates. There will be, accordingly, nitric acid aggregates of uranyl nitrate, uranyl nitrate and chloride aggregates and hydrochloric acid aggregates of uranyl chloride.

(2) Whether there is a gradual change in the frequency of vibration of the absorbers for a series of uranyl or uranous aggregates, or whether there is simply a relative change in the intensity of a number of finer bands which blend so as to form the uranyl or uranous bands, can not be decided from the data now at hand. In the case of the neodymium salts, the latter effect seems to manifest itself in the spectrograms that have been made.

(3) It is probable that the presence of free acid in solvents other than water will lead to the discovery of many new bands of neodymium, erbium, etc. A striking example of this kind is the effect of dissolving hydrochloric acid gas in a neodymium chloride solution in ethyl alcohol. The effect of the free acid

is to bring out very strongly bands at λ 3695 and λ 3760. The presence of sodium perchlorate has a similar effect.

(4) Mixtures of varying amounts of two salts in the same solvent may result in a gradual shift from the bands of one salt into the bands of the other, the shift depending on the amount of each salt present. As an example of this, uranyl sulphate and uranyl nitrate were studied. On the other hand, there are examples where the two salts do not seem to form any intermediate aggregates, and the bands of each simply vary in intensity without showing any change in frequency.

(5) Acid aggregates of uranous salts are found to be much more stable than the neutral aggregates. Uranous nitrate, for instance, is very unstable; but uranous chloride dissolved in concentrated nitric acid (the absorption spectrum is entirely different from that of uranous chloride) will stand for hours before it is oxidized to the uranyl condition. Neutral uranous salts in solution, when heated to 80° or 90°, form a black precipitate; but if some free acid is present (or in the case of uranous chloride if other chlorides are present) the uranous salts are much more stable.

(6) Aggregates form compounds with solvents in many cases (for example, various uranous aggregates in water and methyl alcohol) that are as characteristic as those formed by the pure neutral salt. As yet no work has been done on the effect of temperature and concentration on solvate aggregates.

(7) In discussing the differences in the chemical properties of aggregates, mention will be made of the reduction and oxidation of uranium salts. It is very probable that many other chemical properties differ very much for the various aggregates, but as this work has been mainly concerned with the reduction and the oxidation of the salts, only these properties will be considered. As some of the methods used in the reduction of the uranyl salts are in themselves of considerable interest, they will be taken up in more detail than would otherwise be done.

The method employed for the preparation of the uranous salts for work on absorption spectra has been that described by Jones and Strong.[1] Under these conditions it is possible

[1] Phil. Mag., **19**, 566 (1910).

to obtain quite concentrated solutions of the chloride, the bromide and the sulphate. No aqueous solution of uranous nitrate could be obtained, although small amounts were formed when the hydrogen was first liberated from the acid, but in a very short time the uranous nitrate was oxidized.

The most concentrated solution of any uranous salt thus far obtained is that of the chloride. Uranyl chloride is dissolved in ether (the solution forms three distinct, immiscible layers, the concentration of uranyl chloride in each being different). To this solution is added a small amount of zinc and concentrated hydrochloric acid. The uranous chloride formed is insoluble in ether and accumulates in the dark oily liquid at the bottom of the vessel. Layers of this liquid 1 mm. thick are almost opaque. The reduction of uranyl chloride in isobutyl alcohol is very similar to that in ether.

When hydrochloric acid and zinc are added to a solution of uranyl nitrate a considerable amount of a uranous salt is formed, although it is quickly oxidized again. This is true even when quite large amounts of hydrochloric acid are present. A much more complete spectrographic study of the reduction of uranyl aggregates should be made, as it would probably lead to some knowledge as to how the oxygen atoms are removed from the uranyl group, and of the influence the other atoms and molecules of the aggregate have upon this reduction.

(8) Oxidation reactions also indicate very clearly that different aggregates apparently possess different properties, although the action of the other salts or acids present in the solution may modify the action of the oxidizing agent. However this may be, it is found that uranous acid aggregates require a great deal more of the oxidizing agent, especially when this is hydrogen peroxide, than do the neutral aggregates.

(9) Assuming the presence of aggregates, it is important to know what effect dilution has upon their composition. It would be supposed that the aggregates would break down at high dilution. To test this supposition the absorption spectra of uranyl nitrate and uranyl sulphate were photo-

graphed at very great dilution. If dissociation is sufficiently great it would be expected that the uranyl nitrate bands would shift towards the red with decrease in concentration, and the uranyl sulphate bands would shift towards the violet, so that for very great dilution the uranyl bands of both salts would be identical. This was not found to be the case. There appeared a very slight shift of the uranyl nitrate bands to the red, and possibly a slight shift of the uranyl sulphate bands to the violet; but these shifts were extremely small, so small, indeed, that some observers who looked at the spectrograms did not detect them at all. If the shifts occur, it is exactly what would be expected if the uranyl nitrate and uranyl sulphate aggregates break up into complex ions. The loss of an NO_3 group would cause the uranyl nitrate bands to shift only slightly to the red if the aggregate was of some size, and the same would be true of the uranyl sulphate aggregate. If this theory is true it indicates that the aggregates possess quite a high degree of complexity.

(10) The question has been asked as to whether the aggregates are definite chemical compounds, whether they have a definite composition and how stable they are. Unfortunately the spectroscopic method itself can not solve these problems, but by studying the composition of the acid aggregate precipitates that are often formed, and the chemical composition and absorption spectra of these, much light may be thrown on the subject. The other physical and chemical properties of solutions containing aggregates should also be studied.

The Effect of Temperature on Absorption Spectra

(1) The general effect of rise in temperature is to give a solution of an inorganic salt a deeper color. This deepening of the color signifies that the absorption of light has become more selective, and spectroscopic work indicates that this selective absorption is usually due to a widening of the absorption bands. As these bands are never so distributed over the spectrum as to give a colorless solution, it follows that a widening of the absorption bands will intensify the color of the solution. In many cases this widening appears to be quite

unsymmetrical, but this need not necessarily mean that the center of gravity of the individual absorption band is shifted. Many examples of the neodymium absorption bands show this phenomenon very clearly. For instance, the absorption due to the γ and δ groups of bands may be sufficiently intense to make these groups appear as single bands. If the absorption is not so intense as this, in some solvents it is found that with rise in temperature the shortest wave-length bands may decrease in intensity, and may even disappear. The long wave-length bands increase in intensity, and in some cases new bands appear. Knowing this, it is easy to understand that if the absorption is so strong that each of these groups of bands appears as a single band, these broad bands will widen very unsymmetrically towards the red with rise in temperature. It may be that some change like this takes place in the case of the uranyl bands. It is for this reason that a formula calculated for the widening of a band with rise in temperature would not apply to many wide bands.

(2) In the case of all pure salts dissolved in a single solvent, the bands have been found to widen with rise in temperature, and at the same time they become more diffuse, the edges becoming hazier. When there is a mixture of salts in the same solvent, the bands may become much weaker with rise in temperature. This is the case in a mixture of neodymium and calcium chlorides in water. In a similar manner the absorption of a salt in two solvents probably decreases, in intensity with rise in temperature. An example of this kind is that of uranous bromide in 40 per cent. water and 60 per cent. alcohol. At ordinary temperatures the bands are of about equal intensity. At 80° the water bands have practically disappeared, without the alcohol bands having widened to any great extent.

(3) In general, the center of intensity of single bands changes but little. Whenever there is any change of wave length, the shift is invariably towards the red. It seems that this shift is greater the wider the band, so that it is difficult to say in most cases whether the shift is real or only apparent. In the case of solutions of pure neodymium and erbium salts the shift is, in general, too small to be observed.

(4) A study of gaseous aggregates, such as $N_2O_4 \rightleftarrows 2NO_2$, indicates that raising the temperature or lowering the pressure increases the relative number of the simpler molecules. Many vapors like those of the fatty acids show molecular clustering at low temperatures. In a similar manner it would be expected that aggregates would gradually break down at the higher temperatures. In considering specific examples it would be expected that the breaking down of acid uranyl sulphate aggregates would result in a shift of the uranyl bands, the shift being towards the violet. On the other hand, if the nitric acid uranyl nitrate aggregates are broken down, it would be expected that the uranyl bands would be shifted towards the red. According to this view the shift of the uranyl bands of uranyl nitrate in nitric acid and of uranyl sulphate in sulphuric acid, with rise in temperature, should be quite different if the only effect of rise in temperature is a breaking up of the aggregates.

In advancing a hypothesis of this kind it is assumed that it is only the molecules in an aggregate that are effective in changing the frequency of vibration of the absorbing systems of the light centers. This means that the kinetic energy of the aggregate corresponds to that of a molecule at the same temperature in the solution, the individual molecules in an aggregate all moving together. Whether there is a constant interchange of these molecules and the molecules of the solution, spectroscopic evidence does not as yet show. Neither can it be said with certainty that molecules outside the aggregates do not affect the frequencies of vibration of the absorbing system within the aggregate. Assuming that this is not the case, then it follows of necessity that with rise in temperature the acid aggregates are not broken up, because the uranyl bands of acid solutions are then shifted to the red. This shift seems to be about as great for uranyl sulphate in sulphuric acid as it is for uranyl nitrate in nitric acid. In a similar manner, acid solutions of neodymium salts do not have their absorption spectra changed with rise in temperature so as to resemble more closely that of the neutral salt, as one would expect if the acid neodymium aggregates were broken down.

(5) When foreign salts like calcium chloride are added to solutions of neodymium chloride, it is probable that aggregates containing the two salts are formed. In the case of aqueous solutions of these salts it is found that the neodymium bands are shifted to the red with rise in temperature, whereas aqueous solutions of pure neodymium chloride do not show this effect at all. Exactly what takes place in this case is not evident.

(6) The effect of rise in temperature on solutions showing the solvate bands of equal intensity has been to cause a change in the intensity of the solvate bands; very little, if any, change, however, in the wave lengths of the bands takes place. In the case of water and alcohol, the alcohol bands increase in persistency as the temperature is raised.

(7) In the work with the closed cell at high temperatures it was found that precipitates were formed in practically every case, probably due to hydrolysis, alcoholysis, etc., precipitation taking place in dilute as well as in concentrated solutions. Several examples were tested of concentrated solutions of colored salts mixed with calcium or aluminium chloride, and precipitation was found to take place under these conditions at comparatively low temperatures. It would be very interesting to learn whether acid aggregates of uranyl, neodymium, erbium and such salts are less likely to form precipitates than the neutral salt solutions.

In the case of neutral uranous solutions these precipitates form at 70° or 80°. The presence of acid prevents this precipitation at temperatures below 100°.

Whether the salt precipitation at high temperatures is complete or not can not be decided in general at present. In the case of several neodymium and erbium solutions this seemed to be the case. In one of the uranyl solutions, however, some uranyl salt remained in the solution after the precipitate had settled.

(8) It may be said, in general, that there is a very great increase in the absorption of all solutions in the short wave-length region of the spectrum as the temperature is raised. How great this increase in absorption would be if pure solutions

were used has not yet been determined. The formation of precipitates is usually preceded by a very great increase in the short wave-length absorption.

(9) The problem as to whether a rise in temperature produces a permanent change in the structure of the aggregates in solution has not been studied to any great extent. In the case of the existence of two solvent spectra it is found that the spectra, on cooling the solution, are exactly the same as before heating. In the case of an acetone solution of uranyl chloride it was found that the bands are apparently single after the precipitate was formed during the heating. Whether these bands would have become double again when the solution was cooled was not tested. It would be interesting to learn whether selective solvate precipitation would take place on heating solutions.

(10) It seems worth while to call attention to the promising and important application of spectrophotography at low temperatures to the study of the nature of chemical reactions. As soon as the changes in breadth, intensity and frequency of individual absorption bands and the constitution of the groups of bands can be interpreted, our knowledge of the relation between absorption centers or aggregates and the other physical and chemical units of matter will be much more fully understood, and the changes which these particles undergo will be much better comprehended.

Absorption Spectra and the Solvate Theory of Solution[1]

The first *direct spectroscopic evidence* for the existence of solvates was furnished by Jones and Anderson in their study of salts of neodymium. A salt like neodymium chloride was found to have a very different absorption spectrum in water from what it had in methyl alcohol. Neodymium chloride in the proper mixture of water and methyl alcohol shows both the "water" bands and the "alcohol" bands. By varying the amounts of the solvents relative to one another the relative intensities of the two sets of bands can be changed at will.

[1] This section was written by myself after the remainder of the paper had been prepared.—H. C. J.

Neodymium nitrate in a mixture of water and the alcohol shows bands of the same character in the two solvents as the chloride.

Praseodymium chloride in a mixture of water and methyl alcohol shows the same kind of change as neodymium chloride. In this case an entirely new band appears in the alcohol, which has no analogue in the aqueous solution.

The existence of "water" bands and "alcohol" bands in the aqueous and alcoholic solutions, respectively, is interpreted by Jones and Anderson as direct evidence for the existence of hydrates in the aqueous solutions and of alcoholates in the alcohol solutions—in a word, is direct spectroscopic evidence for the solvate theory.

The largest amount of and most direct spectroscopic evidence for the solvate theory of solution has been brought to light by our work, which has been in progress continuously during the past three years. A careful study was made of the absorption spectra of cobalt salts in different solvents and as affected by temperature. Glycerol solutions of these salts showed a different spectrum from aqueous solutions, indicating the presence of glycerolates in such solutions, as we have hydrates in aqueous solutions.

The effect of rise in temperature is to increase enormously the absorption of concentrated aqueous solutions of cobalt chloride, especially in the red. It is well known that such solutions turn blue on heating. The more concentrated the solution the lower the temperature at which this color change takes place. There is a large amount of evidence which points to the conclusion that this change in absorption is due to a breaking down of the more complex hydrates with rise in temperature. If this is the true explanation of the phenomenon, the presence of a dehydrating agent such as calcium chloride or aluminium chloride ought to cause this change in absorption to take place at a lower temperature, since the dehydrating agent would assist the rise in temperature in breaking down the complex hydrates.

The results here are in accord with prediction. The addition of either of the above chlorides causes the great absorp-

tion in the red to take place in more dilute solutions at the same temperature, or in a given solution at a lower temperature.

It was further found that the temperature at which this marked change in the red absorption takes place is higher for aqueous and glycerol solutions than for solutions in other solvents, showing that the "hydrates" and "glycerolates" are more stable with respect to temperature than other solvates.

The effect of rise in temperature on salts of chromium was also studied, and was shown to be similar to the effect of rise in temperature on cobalt salts—the higher the temperature the greater the absorption.

The action of dehydrating agents on chromium salts was similar to that on salts of cobalt.

Absorption Spectra of Uranium Salts.—A fairly comprehensive study was made of the absorption spectra of uranium salts, to see especially whether there was evidence obtainable for the existence of definite solvate bands in different solvents. We studied both uranyl and uranous compounds.

It was soon found that an aqueous solution of uranyl chloride shows absorption bands in different positions from solutions in methyl alcohol. These differences were sufficiently great to merit careful study.

What these differences are can be seen best by giving in tabular form the wave lengths of a few bands in the different solvents:

Uranyl Chloride

In water	λλ 4025	4170	4315	4460	4560	4740		4920
In methyl alcohol	λλ 4090	4220	4345	4465	4590	4760		4930
In ethyl alcohol	λλ 4100	4250		4400	4580	4750		4900
In propyl alcohol	λλ 4100	4230	4460	4580	4580	4750		4910
In isopropyl alcohol	λλ 4100	4250		4360	4560	4750		
In butyl alcohol	λλ 4100	4240	4390	4560	4750		4970	
In isobutyl alcohol	λλ		4400	4560	4720		4900	
In ether	λλ 4040	4160	4300	4444	4630			
In methyl acetate	λλ 4030	4160	4280	4440	4620	4790		4920
In glycerol	λλ 4025	4140	4260	4400	4540	4720		5050
In formamide	λλ			4450	4650			4840

The absorption spectra of uranyl nitrate in mixtures of water and methyl alcohol were photographed. The absorp-

tion in pure methyl alcohol was much greater than in pure water. As water was added to the alcoholic solution the absorption became less and less. In the mixed solvents the bands became very broad. A careful study of the structure of these broad bands showed that they were coexisting "water" and "alcohol" bands and not one set of bands shifted in position; and this, as we shall see, is an important point.

A simple method of reducing uranyl to uranous salts in solution was found to be the action of nascent hydrogen. This was obtained by introducing into the aqueous solution of the uranyl salt a bar of zinc, and then adding the acid of the salt in question. In this way uranous salts could be prepared, and several of them were found to have sufficient stability for our purpose. Uranous chloride, uranous bromide and uranous acetate were thus made, and their absorption spectra photographed and studied. These salts proved to be very useful for the detection of "solvent" bands, or the effect of the solvent on the absorption spectra of salts dissolved in it. The uranous bands are numerous, and, what is far more important for our work, they are well defined, with comparatively sharp edges, and their wave lengths can be accurately determined. In this respect they are second only to certain lines of neodymium. Some of the most conclusive evidence for solvation in solution furnished by our spectroscopic work was with the uranous salts.

The spectrum of uranous chloride in water is quite different from the spectrum in methyl alcohol, and this, in turn, very different from the spectrum in acetone. A glance at the spectrograms for these solutions would lead us to conclude that we are dealing with three very different absorption spectra.

In a mixture of water and methyl alcohol, as the amount of water increases the water band λ 6750 comes out, gradually increasing in intensity. The methyl alcohol band λ 5050 to λ 4850, which is probably double, narrows on the red side into a band at λ 4850. Methyl alcohol bands λ 4770 and λ 4600 practically disappear and λ 4670 becomes very weak. In their places appear the water bands λ 4700 and λ 4550. The methyl alcohol band λ 4300 to λ 4450 becomes weaker and breaks up

into a band at λ 4400 and a band at λ 4280. The methyl alcohol bands λ 4230 and λ 4120 apparently come together as the amount of water present relative to methyl alcohol increases, and becomes the water band at λ 4160.

It is thus obvious that the aqueous solution shows very different absorption bands from the solution of uranous chloride in methyl alcohol.

The addition of ethyl alcohol to an aqueous solution of uranous chloride produces a very marked change in the spectrum, the ethyl alcohol bands being very different from the water bands. As the amount of ethyl alcohol present relative to water increases, the ethyl alcohol bands come out and the water bands gradually disappear.

The addition of acetone to a methyl alcohol solution of uranous chloride brings out a number of "acetone" bands between λ 6000 and λ 6500. A strong absorption band also appears from λ 6500 to λ 6800. There is also an acetone band at λ 5600.

The addition of acetone to an aqueous solution of uranous chloride produces a marked change in the spectrum, the "acetone" bands being very different from the "water" bands. The acetone solution absorbs much less in the region λ 6500. The aqueous solution has a characteristic band at λ 6750. There are acetone bands at λ 4920, λ 4750 and λ 4590; and water bands at λ 4980, λ 4700 and λ 4570. The absorption of uranous chloride in ethyl alcohol is very similar to the absorption in methyl alcohol, as would be expected, the methyl alcohol bands being of slightly shorter wave lengths.

The absorption spectrum of uranous chloride in glycerol was photographed, also when water was added to the glycerol solution.

The absorption spectrum in glycerol was found to be very different from what it is in water.

The absorption spectrum of uranous chloride in a mixture of methyl alcohol and ether was photographed. The methyl alcohol solution showed complete ultraviolet absorption to wave length λ 3700. The addition of ether increased the ab-

sorption, the absorption of the short wave lengths extending now to λ 3800.

In methyl alcohol there was considerable general absorption in the region λ 4300. With the addition of ether the absorption was almost complete from λ 4100 to λ 4450. The addition of ether caused the uranyl bands to shift slightly towards the red without, however, changing their general character. The magnitude of this shift can be seen from the following table:

Uranyl Chloride Bands in Methyl Alcohol

$\lambda\lambda$ 3880	4000	4110	4240	4400	4610	4780	4930	5050
		4135	4285					

Uranyl Chloride in Methyl Alcohol to which Ether is Added

$\lambda\lambda$ 3890	4010	4140	4260	4440	4630	4790	4960	5050

The effect of the presence of ether is thus very pronounced, not only causing the bands to shift slightly towards the red, but also increasing the amount of absorption.

It should be stated that in the work with the uranous salts there were present in the solution, in addition to the salt, a little of the free acid of the salt and a small amount of the zinc salt. While these probably had a slight effect on the absorption spectra, the effect must have been far too small to have produced such changes as those recorded above for the different solvents.

Having found such abundant evidence for the effect of the solvent on the power of the dissolved substance to absorb light, in the case of the few solvents referred to above, it seemed very desirable to bring other solvents within the scope of this work, and this has been done. Since the neodymium lines and bands are very sharp, this element was selected as the principal substance to be used in studying the effect of the solvent on the absorption spectra of the dissolved substance, where a large number of solvents was to be employed.

Absorption Spectra of Neodymium Salts.—The following nomenclature will be used in describing the neodymium absorption spectra:

α group in the region λ 3400 to λ 3600.
β group at about λ 4300.
γ group from λ 4600 to λ 4800.
δ group from λ 5000 to λ 5400.
ε group in the region λ 5800.
ζ group at λ 6300.

The change in the absorption spectra of neodymium chloride as the solvent is changed can be seen best by expressing the results in the following form. The abbreviations used are: "d" diffuse, "fa" faint, "fi" fine, "h" hazy, "i" intense, "n" narrow, "sh" sharp, "st" strong, "we" weak, "wi" wide.

The results obtained below with neodymium chloride show the effect of the solvent on the absorption spectra of solutions of this compound. The bands of the different solvents have different wave lengths and different relative intensities.

Having found that the solvent played such an important role in determining the absorption of light by the dissolved substance, we used *isomeric organic solvents* to see whether such closely related compounds would affect differently the power of substances dissolved in them to absorb light. We prepared solutions of neodymium chloride in propyl and isopropyl alcohols and in butyl and isobutyl alcohols, and photographed the absorption spectra of this salt in these isomeric solvents. The results below show different absorption lines and bands in the isomeric solvents.

If we compare carefully the spectra of neodymium chloride in butyl and isobutyl alcohols, we find that the bands are weak and diffuse in isobutyl alcohol, and have different relative intensities from what they have in the butyl alcohol. The bands in butyl alcohol are very much finer and sharper than they are in isobutyl alcohol. Further, the bands of neodymium chloride in isobutyl alcohol have slightly greater wave lengths than in butyl alcohol.

To eliminate the possibility of the effect of the solvent on absorption spectra being due to anything inherent in the nature of neodymium chloride, the nitrate of neodymium was studied in the same way as the chloride.

The absorption spectra of neodymium nitrate in water, in

α Group

In water	In methyl and ethyl alcohols	In propyl alcohol	In isopropyl alcohol	In butyl alcohol	In isobutyl alcohol	In glycerol
λλ 3390 we.	λλ 3475 f.	....	....	....	λλ 3455 we.	λλ 3520 we.
3465 n. st.	3475 fa.	λλ 3545 sh.	λλ 3460	λλ 3450 sh. n.	3485 st.	3475 st.
3505 n. st.	3505	3460	3510	3460 we.	3515 we.	3550 st.
3540 n. st.	....	3490	3535	3492 d.	3545	....
3560	3560 wi. i.	3510 we.	....	3535 sh. n.	3570	....
....	....	3525 st.	....	3545	....	....
....	....	3540 st. n.	....	3560 d.	....	....
....	....	3560 d.	....	....	....	....
....	....	3580 we.	....	....	....	....

β Group

λλ 4271 sh.	λλ 4290	λλ 4270 we.	λλ 4265	λλ 4265	λλ 4300 we.	λλ 4288 sh.
4290 n. we.	4325	4285	....	4285	....	4270 fi.
....	....	4330 wi. we.	....	4300	....	4305 fi.
....	....	4450 wi. we.	....	....	....	....

γ Group

λλ 4610 h.	λλ 4700	λλ 4600 we. d.	λλ 4600 d.	....	λλ 4700	λλ 4620
4645 we.	4780	4700	4690	....	4730	4710
4685	4825	4770	4730	....	4780	4730
4755 sh.	....	4830	....	....	4830	4760
4820 n. i.	....	....	....	....	4880 we.	4790
....	....	....	....	....	....	4840

δ Group

In water	In methyl and ethyl alcohols	In propyl alcohol	In isopropyl alcohol	In butyl alcohol	In isobutyl alcohol	In glycerol
λλ 5090 n.	λλ 5125 h.	λλ 5130 wi. d.	λλ 5100 wi. d.	λλ 5085 n.	λλ 5150	λλ 5120 wi. h.
5125 wi. h.	5180 h. fa.	5180 wi. d.	5320 wi. d.	5095 n. we.	5260	5170 n.
5205 i. n.	5220 i. n.	5220	....	5130	5215	5190 n.
5222 i. n.	5245 i.	5230	....	5200	5230	5230
5255 n.	5290 n.	5250	....	5215	5250	5240
5315 fa. h.	5315 fa.	5290	....	5240	5300	5250
....	....	5330 we.	....	5270	....	5270 we.
....	....	....	....	5300	....	....

ε Group

λλ 5725 n. st.	λλ 5725 h.	λλ 5740	λλ 5720 d.	λλ 5750	λλ 5740 we.	λλ 5740 h.
5745 st.	5765 n.	5780	5780	5780	5810 st.	5790
5765 st.	5800 st.	5810	5810	5820	5850 st.	5805
5795	5835 i.	5850	....	5860	5890	5820
....	5860 h.	....	....	5930	5920	5850
....	5895 fa.	....	....	5930	5950 we.	....
....	5925 fa.	....	....	....	5995 we.	....
....	....	....	....	....	6020 we.	....

methyl alcohol, in ethyl alcohol, in mixtures of these alcohols and water, in propyl and isopropyl alcohols, in butyl and isobutyl alcohols, in acetone and in mixtures of acetone and water, in ethyl acetate and in formamide, were carefully photographed and studied. The results are given in the case of neodymium nitrate only for the α bands.

α Bands

In Water.—Practically the same as the bands of neodymium chloride, but the bands of the nitrate are broader and hazier than those of the chloride.

In Methyl and Ethyl Alcohol.—There are only two bands in the α group, λ 3465 and λ 3545.

In Propyl Alcohol.—$\lambda\lambda$ 3455, 3500 and 3585.

In Isopropyl Alcohol.—$\lambda\lambda$ 3460, 3505 and 3535.

In Butyl Alcohol.—$\lambda\lambda$ 3450, 3500 and 3540.

In Isobutyl Alcohol.—Ultraviolet absorption was so great that on the photograph taken the α group did not appear. The absorption in general is the same as that of the chloride in this alcohol.

In Acetone.—$\lambda\lambda$ 3475, 3555.

In Ethyl Acetate.—$\lambda\lambda$ 3455, 3500 and 3540.

The other groups of absorption bands of neodymium nitrate in the different solvents show differences in the wave lengths comparable with the above, but these results suffice to show the effect of the solvent on the power of neodymium nitrate to absorb light.

The above evidence that the solvent plays an important role in the absorption of light by substances dissolved in it is strong. When we take into account the number of salts studied and the number of solvents employed the evidence is little short of proof. The only reasonable question is: How are we to interpret these facts? Before attempting to answer this question we should take into account also the following fact. We have seen that a salt dissolved in a given solvent is characterized by a definite absorption spectrum. When a salt is dissolved in mixtures of varying proportions of two solvents *only two definite absorption spectra appear*, one being

characteristic of each solvent. One spectrum does not gradually change into the other as the composition of the mixed solvent changes, but only the *relative intensities* of the two spectra vary. Starting with that mixture of the two solvents in which both of the spectra are equally intense, if we diminish the amount of *a* relative to *b*, the spectrum corresponding to *a* becomes feebler and feebler and the spectrum corresponding to *b* more and more intense. This fact was first noted by Jones and Anderson,[1] and has since been repeatedly confirmed by our work. We found that when neodymium chloride is dissolved in a mixture of methyl alcohol and water, it showed a definite set of "water" bands and a definite set of "methyl alcohol" bands. As the amount of water in the solution was decreased relative to the alcohol, the "water" bands decreased in intensity but remained in the same position. As the amount of alcohol in the solution was decreased relative to the water, the "alcohol" bands decreased in intensity, but their position remained unchanged.

Jones and Anderson interperted these facts as strong evidence in favor of the view that there are definite hydrates and definite alcoholates in the solution.

The spectroscopic evidence for solvation in solution furnished by Jones and Anderson has, as has already been stated, been increased manyfold by our work. A large number of solvents and a fairly large number of salts have been used, and the existence of solvent bands in general established.

Relative Stability of the Different Solvates

The question of the relative stability of the different solvates with respect to various physical and chemical agents has been studied at length, by means of absorption lines and bands.

(1) The percentage of solvents for which each set of solvent bands has the the same intensity will be used as a measure of the "persistency" of the given solvates. The "persistency" of any given solvate will vary inversely as the proportion of that solvent that is necessary for the bands to appear

[1] THIS JOURNAL, **41**, 276 (1909).

of a given intensity. Whether there is any relation between the persistency of solvate bands and the absolute values of a and b is not known.

(2) The persistency of the same solvate bands for different salts is quite different. In the case of neodymium chloride in water and alcohol the bands are of the same intensity when 8 per cent. of water and 92 per cent. of alcohol are present. In the case of samarium chloride a smaller percentage of water is required, the water bands of samarium chloride having a greater persistency than the water bands of neodymium chloride. The persistency of the water bands of neodymium nitrate is different from those of the chloride. In the case of the uranous salts the water bands are much less persistent, the water and alcohol spectra being of about the same intensity when there is about 40 per cent. of water and 60 per cent. of alcohol present.

(3) The persistency of the bands of the same salt in different solvents is very different. In general, the "*water*" *bands are the most persistent of all the solvent bands at ordinary temperatures.*

(4) The persistency of solvent bands depends on the concentration of the solution. Keeping the percentage of water and alcohol constant, it is found that the alcohol bands of neodymium chloride and of the uranous salts are relatively more persistent for the greater dilutions, i. e., Beer's law does not hold for solutions containing two solvents.

(5) Very little work has been done on the change in the persistency of solvate bands when foreign salts are added to the solution. The addition of aluminium and calcium chlorides to solutions of colored chlorides seems to increase the persistency of the alcohol bands relative to the water bands.

(6) The selective action of foreign salts on solvates is shown very strikingly by the addition of oxidizing agents to solutions of uranous salts in water and alcohol. Substances like potassium and calcium nitrates and sodium perchlorate cause the water bands to decrease very greatly in intensity. The alcohol bands, on the other hand, seem to remain of about the same intensity. Whether this is due to the oxidation of the hy-

drate or simply to a decrease in its persistency cannot always be stated. Some cases indicate that selective oxidation takes place. The oxidation of hydrogen peroxide affects water and alcohol bands in the same way.

(7) In many cases the solubility of a salt like uranous bromide is much less after alcohol has been added to the water than before. Sometimes precipitates form when a second solvent is added, and in some cases the filtrate shows the presence of only one solvate, whereas before the precipitate was formed both solvates were present. This may be denoted as selective solvate precipitation.

(8) The effect of rise in temperature changes the relative intensity of the solvate bands of a solution. A very marked example of this kind is a solution of uranous chloride in a mixture of water and ethyl alcohol in such proportions as to show the water and alcohol bands of the same intensity at ordinary room temperatures. Heat the solution to about 80° and the water bands practically disappear, leaving only the uranous alcohol bands in the spectrum.

(9) Whether or not there is a dynamic equilibrium of solvates is not certain, but the selective action of foreign salts, the effect of changing the relative quantities of the solvents and of changing the temperature would lead us to believe that there is some interchange of solvates going on. The velocity of reactions of this kind may, however, be comparatively slow.

Taking all of the spectroscopic work into account, the evidence from this source strongly supports the solvate theory of solution as advanced in this laboratory more than a dozen years ago. The bearing of this theory upon chemistry and other branches of natural science has already been pointed out.[1]

We are now studying in this laboratory the effect of ions as compared with molecules on the absorption spectra of solutions, the effect of high temperature on the absorption spectra of aqueous solutions, and the measurement of the intensi-

[1] THIS JOURNAL, **45**, 146 (1911). Z. physik. Chem., **74**, 377 (1910). J. chim. phys., **9**, 217 (1911).

ties of the various absorption bands by means of the radiomicrometer and thermoelectric junctions.

In conclusion, we wish to express our thanks, especially, to the Carnegie Institution of Washington for the generous support which they have given this work in the past, and for the aid which they have tendered for the future. We wish to thank Professor Ames for ample space in the Physical Laboratory for doing the physical part of this work. We would also express our thanks to Professor Anderson and to Professor Pfund for valuable suggestions in connection with the work, and to Dr. Guy, who will continue this work, for aid especially in preparing the various salts and solutions of salts of dysprosium and samarium.

DESCRIPTION OF PLATES

Plate XIX. *A.* Neodymium Chloride in Methyl Alcohol. Concentration, 0.1 normal. Depth of cell, 10 cm. Temperatures, 26°, 40°, 55°, 78° and 85°.

B. Neodymium Bromide in Methyl Alcohol. Concentration, 0.1 normal. Depth of cell, 10 cm. Temperatures, 25°, 35°, 44°, 60°, 82°, 100° and 120°. At the highest temperatures a precipitate was formed.

Plate XX. *A.* Neodymium Bromide in Water. Concentration, 1.66 normal. Depth of cell, 1.0 cm. Temperatures, 20°, 40°, 60°, 80° and 93°.

B. Neodymium Chloride in Water. Concentration, 2.05 normal. Depth of cell, 1.0 cm. Temperatures, 20°, 50° and 75°.

Neodymium Nitrate in Water. Concentration, 2.15 normal. Depth of cell, 1.0 cm. Temperatures, 20°, 75° and 95°.

Plate XXI. *A.* Neodymium Chloride in Acetone, 10° and 70°.

Neodymium Chloride in Ether, 10°.

Neodymium Chloride in Ethyl Alcohol, 10° and 70°.

Neodymium Chloride in Ethyl Alcohol and Hydrochloric Acid at 10° and 70°.

B. Neodymium Nitrate in Nitric Acid, 10° and 50°.

Neodymium Chloride in Water (8 per cent.) and Methyl Alcohol at 10° and 70°.

Neodymium Nitrate in Water (8 per cent.) and Acetone at 10° and 60°.

Neodymium Chloride in Water (40 per cent.) and Ethyl Alcohol at 10°.

Neodymium Chloride in Water (40 per cent.) and Glycerol at 10°.

Plate XXII. *A*. Neodymium Chloride in Water at 10° and 90°.
Neodymium Chloride in Hydrochloric Acid at 10° and 90°.
Neodymium Chloride in Methyl Alcohol.
Neodymium Chloride and Sodium Chlorate in Methyl Alcohol.

B. Neodymium Acetate in Water at 10° and 90°.
Neodymium Chloride in Acetic Acid at 10° and 90°.
Neodymium Acetate in Acetic Acid at 10° and 90°.
Neodymium Acetate in Methyl Acetate and Acetic Acid at 10° and 90°.

Plate XXIII. *A*. Erbium Chloride in Water at 20°, 30°, 85° and 115°.

B. Neodymium Chloride in Water. Concentration, 0.2 normal. Depth of cell, 10 cm. Temperatures, 20°, 50°, 85° and 115°.

C. Neodymium Nitrate in Tertiary Butyl Alcohol. Concentration, 0.2 normal. Depth of cell, 1.0 cm. Temperatures, 25°, 50° and 65°.
Neodymium Nitrate in Isobutyl Alcohol at 20°, 75° and 100°.

Plate XXIV. *A*. Uranyl Chloride in Methyl Acetate. Concentration, 0.005 normal. Depth of cell, 10 cm. Temperatures, 20°, 45°, 70°, 90°, 110°, 135° and 140°.

B. Uranyl Nitrate in Propyl Alcohol. Concentration, 0.005 normal. Depth of cell, 10 cm. Temperatures, 20°, 40°, 65°, 85°, 105°, 115°, 130° and 145°.

Plate XXV. *A*. Uranous Sulphate in Sulphuric Acid at 10° and 90°.
Uranous Sulphate in Water at 10° and 90°.
Uranous Chloride in Water and Methyl Alcohol at 10° and 70°.

B. Uranyl Nitrate in Nitric Acid at 10° and 70°.
Uranyl Chloride in Hydrochloric Acid at 10° and 80°.
Uranyl Sulphate in Water at 10° and 80°.
Uranyl Sulphate in Sulphuric Acid at 10° and 70°.

JOHNS HOPKINS UNIV.
June, 1911

REVIEWS

THE TECHNOLOGY OF BREAD-MAKING, including the Chemistry and Analytical and Practical Testing of Wheat, Flour and Other Materials employed in Bread-making and Confectionery. By WILLIAM JAGO, F.I.C., F.C.S., of Lincoln's Inn, Barrister-at-Law, Senior Examiner in Bread-making and Confectionery to the City and Guilds of London Institute for the Advancement of Technical Education, etc., and WILLIAM C. JAGO, Food Manufacturing Chemist. American Edition. Chicago: Bakers' Helper Co. pp. viii + 908.

The earlier editions of Jago's "Technology of Bread-making" have long been recognized as classics in this field. The new American edition of this work, under the joint authorship of Wm. and Wm. C. Jago, will, therefore, be welcomed by every one who is interested in the chemistry and technology of wheat and its products, as well as by students of dietetics and kindred subjects.

The authors announce that in the preparation of the work "the requirements of the student of technology, whether baker or miller, have been the first consideration. In addition the authors have endeavored to make the book as complete a work of general reference as possible." The second purpose has certainly been accomplished to a remarkable degree. The detail and depth of scientific treatment of the subject are, however, quite beyond the range of knowledge of the average technologist, the work covering the field to the limits required by the most exacting student.

The book is a heavy volume of 892 pages of closely printed matter, interspersed with a limited number of well-chosen but generally rather poorly-made illustrations. The first fifty-six pages are devoted to a very excellent attempt to accomplish the impossible task of a general survey of the whole field of inorganic and organic chemistry, showing a fine discrimination in the facts selected as essential to a comprehension of the technical phases of the subject. The next sixty pages are devoted to a careful detailed discussion of the chemical constituents, of wheat and flour. This is followed by one hundred and thirty-six pages of remarkably clear and complete discussion of fermentation in general and yeast action in particular, constituting the best and most practical presentation of this field from the technical standpoint that has come to the writer's notice. Forty pages are given to the physical structure and chemical composition of the wheat kernel. The next one hundred and ten pages are devoted to flour, including two unusually valuable chapters on "Strength of Flour" and "Bleaching of Flour," in which the recent elaborate re-

searches on these subjects are fully and impartially reviewed. The general discussions of "Bread and Bread-making" cover one hundred and eighty pages and include, in addition to the usual subject matter, very interesting chapters on "Wheat, Flour and Bread Improvers" and on the legal aspects of "Weighing of Bread," the latter, however, from the English rather than the American point of view. The technology of commercial bread-making is treated in careful, exact, and interesting detail, in one hundred pages, the illustrations in this division of the work being more numerous and better made than in any other part of the book. The remaining two hundred and ten pages are devoted to a thoroughly up-to-date description of methods of laboratory tests and analyses and of routine mill tests of wheat, flour and confectioner's raw materials.

As a whole, the book is a practically complete reference library of the present-day knowledge of this subject. It is up-to-date, containing abstracts of every article of note having any bearing upon the general subject of bread-making which has appeared in current literature up to and including most of the year 1910. These abstracts are characterized by impartial preparation and presentation, and the authors' comments are thoroughly fair and intelligent. References are given in parentheses in the body of the text.

The few directions for "experimental work" which accompany some of the chapters are so brief and cover the fields so incompletely that they can scarcely be regarded as more than casual illustrative material. The book is clearly not intended as a manual for experimental study, but as a reference work, reporting the result of such study by the skilled scientists of the world. As such it has no equal in current literature.

The mechanical make-up of the volume might have been improved, although perhaps not without increasing the cost to an undesirable degree. It would seem to the writer, however, that a work whose general excellence fits it for as extensive and constant reference use as this will undoubtedly receive should be thoroughly well made, and as well bound as possible.

R. W. THATCHER.

ELEKTROCHEMISCHE UMFORMER (GALVANISCHE ELEMENTE). Von JOHANNES ZACHARIAS, Ingenieur. (Elektrotechnische Bibliothek. Bd. LXVI.) Mit 122 Abbildungen. Wien und Leipzig: A. Hartleben's Verlag, 1911 S. xii + 262. Preis: geh., M 4; geb., M. 5.

The title is the author's suggestion of a general term to embrace all types of primary electric batteries. The work is generally descriptive in character, and is in fact a member

of an "electro-technical" library. A brief history of the development of the primary battery is given, including outlines of a number of patents. The origin and manufacture of carbon graphite, zinc and the depolarizing oxides are also described.

The sub ect matter is in two broad divisions, "weak current" and "heavy current" batteries. Of the former many varieties of the common zinc-copper and zinc-carbon elements are accurately described. Dimensions of various parts are given, together with descriptions of methods of manufacture, and the objects aimed at by peculiarities of individual types. The descriptions of dry cells are particularly thorough. In many instances accounts of tests with accompanying performance curves are given. Methods of test and measurement are given at some length. There is much repetition in this chapter, which is also padded with forty pages of rules and specifications of the German Post Office governing the use of batteries in telegraph and telephone service.

The chapter on heavy current batteries describes well the methods used to prevent polarization and increases the output of the simpler weak-current element. While the types described are limited to those of German manufacture, the number of examples and method of treatment are such as to cover the principles and essentials satisfactorily.

The first thirty pages are devoted to an incoherent complaint of the absence of a common foundation and first principles of all physical and chemical theory. The reader's expectations are aroused by a promise to develop a new theory of chemical-electrical transformation starting from simple mechanical principles. The promise is not fulfilled, however, and vanishes in a few vague paragraphs on ether pressure, electric oscillations, resonance and interference of atomic vibrations. The author modestly assures us that he first discovered and explained the impossibility of action at a distance. All serious treatment by theory is absent, but beginning with the third chapter the reader may acquire much information as to the type, sizes and performance of present-day primary batteries.

J. B. WHITEHEAD.

DIE INDIREKTEN METHODEN DER ANALYTISCHEN CHEMIE. Von PROF. DR. JUAN FAGES Y VIRGILI in Madrid. Mit Genehmigung des Verfassers deutsch herausgegeben von DR. WERNER MECKLENBURG, in Clausthal i. H. Sammlung chemischer und chemisch-technischer Vorträge, begründet von F. B. AHRENS und herausgegeben von PROF. DR. W. HERZ. XVI. Band, 11/12 Heft. Stuttgart: Verlag von Ferdinand Enke. 1911. pp. 423–492. Price: M. 1.20.

In this monograph, which probably constitutes the most careful mathematical study that has ever been made of the

indirect processes used in analytical chemistry, the author shows how hard it is to find indirect methods that are wholly satisfactory and concludes that it is wisest at present to seek to improve the direct methods of analysis rather than to devise ingenious processes which do not offer ordinary precision. All the various types of indirect analysis are referred to a single mathematical equation, and it is pointed out how the precision is to be determined. It is shown, by concrete examples, that published analyses of experienced chemists bear witness to the correctness of the mathematical deductions. The mathematical treatment is simple and easy to follow.

W. T. H.

ANLEITUNG FÜR DAS PRAKTIKUM IN DER MASSANALYSE und den massanalytischen Bestimmungen des deutschen Arzneibuchs V. Verfasst von DR R. WEINLAND, a. o. Professor an der Universität Tübingen. Dritte, neu bearbeitete Auflage. Mit 3 Abbildungen. Tübingen: Verlag von J. C. B. Mohr (Paul Siebeck). 1911. S. viii + 156. Preis, geh., M. 3.20; geb., M. 4.50.

The book is intended as a text and laboratory guide for students of medicine and pharmacy but contains so much of a general nature that it should be of interest to all students of analytical chemistry. The principles of volumetric analysis are clearly stated and the treatment of the complicated theory of indicators is thoroughly modern. The methods are based for the most part on the "Arzneibuch V" but are treated broadly enough to be generally useful. The plan of placing interrogation points after statements of fact and incorporating study questions in the text may be suggestive to the student but is distracting to the general reader. A large number of references cover the literature to May, 1911.

R. S. WILLIAMS.

LABORATORIUMSBUCH FÜR DIE INDUSTRIE DER OELE UND FETTE. Von DR. J. MARCUSSON, Ständiger Mitarbeiter am königl. Materialprüfungsamt Berlin. Mit 21 Abbildungen und 20 Tabellen. Laboratoriumsbücher für die chemische und verwandte Industrien. Band XIV. Halle A. S.: Verlag von Wilhelm Knapp. 1911. pp. 12 + 146. Price, M. 6.60.

This is another of the excellent handbooks published by Knapp dealing with the organic oils, the mineral oils having been covered by Kissling.

The book will serve admirably as an introduction to the compendious treatises—a laboratory handbook—and gives clearly and concisely all the principal methods for testing the fats and oils. The first part considers the general properties, composition of and chemical changes taking place

in the fats and oils; the second part deals with their analysis; while the third section treats of the technical products obtained from them, as candles, wool oils, soaps, varnishes, lacquers and lubricants. A. H. GILL.

SUBJECT LIST OF WORKS ON CHEMISTRY (INCLUDING ALCHEMY, ELECTROCHEMISTRY AND RADIOACTIVITY) IN THE LIBRARY OF THE PATENT OFFICE. London: The Patent Office. 1911. pp. iv + 214.

The authors, date and place of publication, number of pages and size of the books, pamphlets and periodicals in the Library of the English Patent Office, grouped under subjects, are given, and even to persons who have not access to the library the list should prove very useful in finding what has been published on any given subject. C. A. R.